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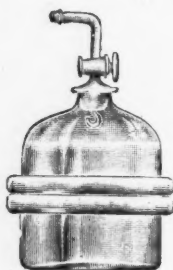
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ADSORPTION AND REPLACEMENT OF PLANT FOOD IN COLLOIDAL OXIDES OF IRON AND ALUMINUM

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University of Maryland

Received for publication July 3, 1922

INTRODUCTION

The work by Wiley and Gordon (1) on colloidal silica and by Starkey and Gordon (2) on different soil colloids under a varying hydrogen-ion concentration, made it of interest to make a more extensive investigation with the colloidal oxides of iron and aluminum. It was first purposed to prepare colloidal oxides of iron and aluminum so that they would obtain nothing other than a trace of the chloride, and find their maximum adsorption from some of the solutions that are commonly used in plant nutrition work; and secondly, to find the necessary conditions for the replacement of this plant food.

MATERIAL USED

Ferric and aluminum hydrogels were prepared by treating hot solutions of ferric chloride and aluminum chloride, respectively, with ammonium hydroxide and washing the resulting hydrogels, with distilled water until there was no test for ammonia or chloride. The hydrogels containing about 96 per cent water were then placed in a glass-stoppered jar. The gels were prepared in sufficient quantities so that one preparation answered for all the subsequent experiments.

Only the hydrogel was used in this work for it was believed that any salt that would allow a hydrosol to exist in the soil would produce a peptization of the hydrogel. The amount of peptization varied with the different salts used, but was very highly marked in the case of the hydrogel of iron when treated with potassium acid phosphate.

The salts were the same as those used with colloidal silica; namely, calcium acid phosphate, calcium sulfate, calcium nitrate, magnesium acid phosphate, magnesium sulfate, magnesium nitrate, potassium acid phosphate, potassium sulfate, and potassium nitrate.

METHODS

Approximately 0.1 *N*, .05 *N* and .025 *N* solutions of the above named salts were prepared by weighing out the calculated amounts of the salts and then determining the exact concentrations. The calcium was determined by precipitating with ammonium oxalate in a solution slightly acid with acetic acid, washing the precipitate, dissolving it in sulfuric acid, and then titrating the resulting solution with potassium permanganate. The magnesium was determined as $Mg_2P_2O_7$, and the potassium was determined as K_4PtCl_6 . Phosphates were determined by precipitating in nitric acid solution with ammonium molybdate, and titrating with

standard sodium hydroxide. Sulfates were determined as BaSO_4 . Nitrates were reduced with powdered iron and sulfuric acid, distilled with sodium hydroxide, and measured by titrating the ammonia.

In the determinations, 400 cc. of the respective solutions were shaken with definite portions of the hydrogels until equilibrium was established. The amount of the iron hydrogel used was that which would correspond to three grams of the gel when it had been dried to a constant weight at 110°C ., while in the case of the aluminum only enough hydrogel was added to correspond to one gram of the dry material. The water added with the hydrogel was figured as water of dilution in calculating the original concentration of the solution. In most cases the mixtures were thoroughly shaken by hand for one minute at intervals of one hour. At the end of the first day, and at subsequent intervals as indicated in the table 2, aliquots of the solutions were taken and their concentrations determined. The shaking was continued until there was no further change in concentration. The total change in concentration gave the total adsorption.

RESULTS

Table 1 shows that there was only a slight adsorption of nitrates in the order of calcium, magnesium, and potassium. With the aluminum hydrogel, no

TABLE 1
Adsorption of nitrates and sulfates by the colloidal oxides of iron and aluminum

SALT USED	METAL ADSORBED BY 1 GM. GEL			NEGATIVE ION ADSORBED BY 1 GM. GEL		
	0.025 N	0.05 N	0.1 N	0.025 N	0.05 N	0.1 N
<i>Iron hydrogel</i>						
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
KNO_3	None	None	None	None	None	None
$\text{Mg}(\text{NO}_3)_2$	1.7	2.2	3.4	6.0	7.0	19.0
$\text{Ca}(\text{NO}_3)_2$	2.2	3.4	8.4	6.6	8.4	21.7
K_2SO_4	2.1	3.5	4.0	3.4	4.3	5.9
MgSO_4	4.8	5.8	7.1	19.3	23.2	28.3
CaSO_4	15.0			35.3		
<i>Aluminum hydrogel</i>						
	3.7	7.5	9.2	4.4	8.4	12.1
K_2SO_4	6.1	8.7	14.6	29.6	41.4	65.9
MgSO_4	19.2			46.0		
CaSO_4						

adsorption of the nitrates of these three metals could be observed. Where adsorption takes place in either gel, approximately equivalent amounts of the ions of the same salt were adsorbed. The small solubility of calcium sulfate has limited its use to one concentration, but even then the amount of adsorption was greater than in the more concentrated solutions of potassium and magnesium sulfates. The adsorption of potassium and magnesium sulfates increased with an increase in concentration. The results with the sulfates indicates that the order of adsorption is calcium, magnesium, potassium.

Experiments were next tried where phosphate solutions were used instead of sulfate. Here the adsorption was found to be much greater, and it took much

TABLE 2
Adsorption of phosphates by colloidal ferric oxide

SALT USED	TIME	METAL ADSORBED BY 1 GM. GEL			PO ₄ ADSORBED BY 1 GM. GEL		
		0.025 N	0.05 N	0.1 N	0.025 N	0.05 N	0.1 N
	days	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
KH ₂ PO ₄	1	21.9	51.7	88.0	121.9	214.4	311.5
	3	27.9	62.3	99.7	133.3	240.8	344.4
	7	37.5	69.3	103.7	141.7	255.5	380.8
	14	40.6	70.5	107.2	143.4	265.4	411.1
	21	40.6	70.5	107.2	143.4	265.4	411.1
MgH ₄ (PO ₄) ₂	1	19.3	31.8	37.6	143.8	242.9	294.0
	7	20.4	33.4	42.5	153.0	265.0	332.2
	14	21.0	34.3	46.7	158.0	275.3	358.6
	21	21.5	36.3	47.4	162.1	281.5	367.5
	28	21.5	36.3	47.5	162.1	281.5	367.5
CaH ₄ (PO ₄) ₂	1	43.0	61.4	82.7	205.8	302.7	402.1
	3	46.5	69.8	100.6	231.3	345.2	485.0
	7	48.9	71.4	103.3	242.7	377.4	550.3
	14	51.3	78.8	113.7	259.4	402.6	574.6
	21	54.3	79.8	116.9	266.6	408.4	586.2
	28	54.5	82.4	120.4	266.6	411.3	597.9
	35	54.5	83.3	121.6	266.6	421.6	607.2
	42	54.5	83.3	121.4	266.6	421.6	609.9

TABLE 3
Adsorption of phosphates by colloidal alumina

SALT USED	TIME	METAL ADSORBED BY 1 GM. GEL			PO ₄ ADSORBED BY 1 GM. GEL		
		0.025 N	0.05 N	0.1 N	0.025 N	0.05 N	0.1 N
	days	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
KH ₂ PO ₄	1	5.5	22.4	46.8	137.7	194.7	284.5
	3	14.0	36.4	69.7	186.4	250.5	356.1
	4	14.0	38.8	74.3	186.4	250.5	356.1
MgH ₄ (PO ₄) ₂	1	12.1	15.5	19.3	164.4	264.5	316.3
	7	15.4	21.0	26.5	251.9	333.7	414.6
	14	17.2	24.1	29.8	260.5	356.7	444.8
	21	17.2	24.4	30.0	260.5	356.7	447.8
CaH ₄ (PO ₄) ₂	1	8.8	17.2	23.2	169.7	236.3	305.0
	3	32.7	51.4	84.9	272.6	393.4	610.2
	4	32.7	51.4	84.9	272.6	393.4	610.2

more shaking to establish equilibrium. These facts are more clearly brought out in tables 2 and 3, and by figures 1 and 2.

By using a continuous mechanical shaking process in the case of calcium and

potassium acid phosphates with aluminum hydrogel, the time required to establish equilibrium was cut down from six weeks to three days. Practically the same final equilibrium point was reached whether shaken by hand or by machine.

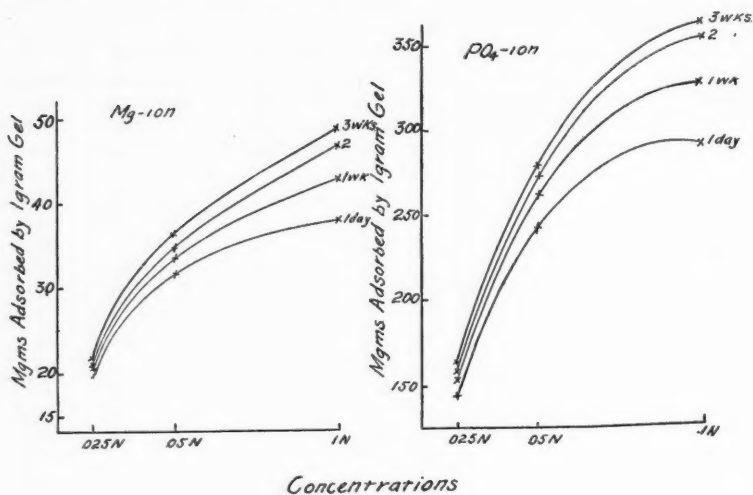


FIG. 1.

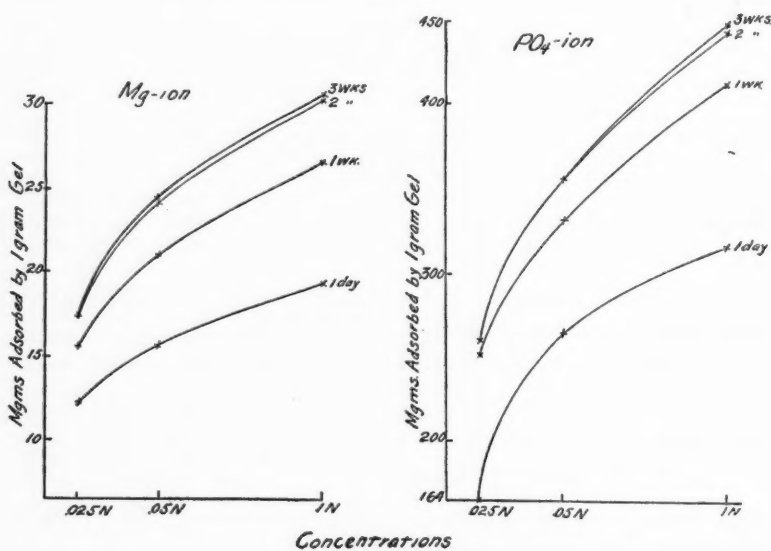


FIG. 2

The curves in figures 1 and 2 show how the adsorption varies with an increase of concentration. It can be observed by the tables that the other salts would give curves similar to the magnesium acid phosphate curves.

The slow establishment of the true equilibrium might be explained by the fact that the equilibrium occurs in two stages; first, the diffusion of the salt in the water contained in the hydrogel, and, second, adsorption itself. It is quite likely that the structure of the gel would prevent a rapid homogeneous distribution of the salt.

The adsorption of phosphates is much more marked by each hydrogel than was the case with the sulfates. In case of the iron hydrogel both ions were adsorbed in approximately equivalent amounts, but the aluminum hydrogel showed a greater adsorption of the phosphate ion than of the metallic ion. The order of the adsorption was the same as in the case of the sulfates.

After finding this marked adsorption of certain plant nutrition salts by the hydrogels, it became of interest to try to release the salts. In view of this the gels which had suffered their maximum adsorption from a .05 *N* solution of calcium acid phosphate were washed successively with 50-cc. portions of distilled water. After each 500 cc. of water had passed through the gel, a 50-cc. portion of the filtrate was taken for analysis. The adsorbed nitrates were quickly washed out, the sulfates less quickly, while the phosphates were held persistently, as shown in tables 4 and 5.

The gels thus washed were further leached with certain solutions of acids, bases and salts. The salts used were .05 *N* solutions of calcium, magnesium and potassium sulfates. Analysis of the filtrates showed that no adsorbed material was released by these washings. This was expected since calcium acid phosphate is made up of the two ions which had suffered the greatest adsorption, and hence should not have been released by the less strongly adsorbed sulfate salts.

The acids and bases gave more varied results; .01 *N* solutions of sodium hydroxide, ammonium hydroxide, calcium hydroxide, citric acid, and a saturated solution of CO_2 were used for washing the gel and successive 50-cc. portions of the filtrate were analyzed. The results are given in table 6.

In case of aluminum all the washings show an increase which rises rapidly in some cases and then decreases. In the washings with sodium hydroxide, ammonium hydroxide and citric acid, the gel was peptized, passing through into the filtrate, and this undoubtedly accounted for at least part of the amount of phosphate in the filtrate. The calcium hydroxide and carbon dioxide solutions gave no peptization, and the increased phosphate in the filtrate was much less marked than in the case of the sodium hydroxide, ammonium hydroxide and citric acid.

There was only slight peptization in the case of iron gel and no marked increase of phosphate in 50-cc. portions of the filtrate. Sodium hydroxide and ammonium hydroxide both slightly increased the phosphate content of the filtrate while there was no increase at all with calcium hydroxide.

It had been found, as stated above, that sulfates failed to release any phosphate and it was further stated why this was anticipated. Conversely, it was suspected that the phosphate would release the sulfates, and hence the replacement of sulfates by phosphates was next tried. Two-hundred cubic centimeter of .05 *N* solutions of potassium sulfate, magnesium sulfate and calcium sulfate were placed in glass stoppered bottles, the equivalents of 1 gm. of dry gel added and the solutions were shaken until equilibrium was established. The adsorption of sulfates was determined, and then sufficient dry magnesium acid phosphate was added to make each solution .05 *N* in regard

TABLE 4
Quantity of phosphate found in 50 cc. portions of filtrate

FILTRATE NUMBER	PO ₄ IN 50 CC. OF FILTRATE FROM THE HYDROGELS AT THE END OF 500-CC. WASHINGS	
	Iron	Aluminum
	mgm.	mgm.
1	6.0	10.0
2	3.2	6.4
3	1.5	2.5
4	1.3	2.1
5	1.2	1.6
6	1.0	1.2
7	0.8	1.1
8	0.7	1.0
9	0.7	0.7
10	0.6	0.4

TABLE 5
Quantity of phosphate washed from gel

	PO ₄ ADSORBED BY HYDROGEL OF FERRIC OXIDE	PO ₄ ADSORBED BY HYDROGEL OF ALUMINA~
	mgm.	mgm.
Before washing.....	259.0	162.4
After washing.....	164.0	117.5

to the latter salt. Equilibrium was again established by shaking and the adsorption of each ion in the solution determined. The results are given in table 7.

Table 7 shows that the sulfate ion was entirely replaced by the phosphate ion in both hydrogels. The phosphate ion was less adsorbed by the aluminum gel in the presence of the sulfate radical than when not in the presence of it, except in the case of calcium sulfate, where it was slightly greater. This may have been due to the influence of the calcium ion which is the most strongly adsorbed of the positive ions used. In the case of the iron gel there was an increase of adsorption in the presence of the sulfates over that found when the

same concentration of magnesium acid phosphate was used alone. This increase was greatest in the presence of calcium sulfate and least in the presence of potassium sulfate.

Since the adsorption varied with concentration as shown in table 3 it became of interest to take a 0.1 *N* solution, obtain the maximum adsorption from it by the hydrogels and then dilute the solution to .05 *N* and determine whether this corresponded to the adsorption from a solution which was originally .05 *N*. This was carried out with solutions of magnesium sulfate, magnesium acid phosphate, calcium acid phosphate, and potassium acid phosphate. The results showed that the equilibrium applied only to the portion of the phosphate

TABLE 6
PO₄ removed by washing the hydrogels of alumina and ferric oxide with 50 cc. portions of acid and basic solutions

FIL- TRATE NUMBER	HYDROGEL OF ALUMINA					HYDROGEL OF FERRIC OXIDE				
	NaOH	NH ₄ OH	Ca(OH) ₂	Citric acid	Sat. sol. CO ₂	NaOH	NH ₄ OH	Ca(OH) ₂	Citric acid	Sat. sol. CO ₂
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
1	8.1	5.4	1.4	2.5	7.7	4.1	2.5	0.0	0.8	0.6
2	11.3	6.5	2.0	4.1	8.6	10.2	5.5	0.0	0.7	0.6
3	12.2	7.8	1.8	11.6	16.0	12.3	6.6		0.7	0.6
4	13.0	8.4	1.8	14.9	16.2	11.5	5.5		0.7	0.5
5	12.3	9.9	1.7	12.7	17.3	11.2	4.4			
6	12.3	9.4	1.6	12.2	16.0	10.0	4.2			
7		7.6	1.9	10.2	17.6	7.0	4.0			
8		6.0	1.8	7.1		3.5	3.5			
9		6.0					3.0			
10							2.5			

which might be leached from the gel as given in table 5, *i.e.*, the equilibrium applied only to 95.0 mgm. of the PO₄ adsorbed by the iron gel and 44.9 mgm. in case of the aluminum gel.

DISCUSSION

In these experiments it has been quite evident that the amount of adsorption depends on how much the coagulated colloid was exposed to the solution. It is probable that the quantity of precipitating electrolyte in the case of colloids has been a varying factor because of the varying speed at which electrolytes are absorbed. The difference in the time required for establishing equilibrium in the case of sulfates and phosphates would bear out this statement.

The nitrates are practically not taken up at all by either hydrogel; hence, it is evident that there can be neither absorption nor chemical reaction between the salt and the hydrogel. In the case of the iron hydrogel we find that the ions are taken up in nearly equivalent quantities, and, hence, it is reasonable to suppose that there must be an adsorption of the molecule as a whole. The

aluminum hydrogel offers a different case, for here we find the phosphate ion taken up in considerable excess of its equivalent of the metal ion with which it is associated.

Much of the data on sulfates and phosphates with both the iron and aluminum hydrogels seems to bear out the theory of selective adsorption. On the other hand when one comes to such results as shown in table 5, one cannot help but believe that there is a chemical force exerting itself. The data shown in table 6 leads one further to believe that this plant food may become useful for plant food by peptization of colloidal gel or by the replacement of one radical by a more strongly adsorbed radical, as shown in table 7.

TABLE 7
Replacement of adsorbed SO_4 by PO_4 in gels

	ALUMINA HYDROGEL						FERRIC OXIDE HYDROGEL					
	K_2SO_4		MgSO_4		CaSO_4		K_2SO_4		MgSO_4		CaSO_4	
	K	SO_4	Mg	SO_4	Ca	SO_4	K	SO_4	Mg	SO_4	Ca	SO_4
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
Before adding $\text{MgH}_4(\text{PO}_4)_2$	11.0	19.0	6.2	26.3	5.7	12.0	11.4	13.6	7.6	31.1	12.9	36.0
After adding $\text{MgH}_4(\text{PO}_4)_2$	16.1	None	11.1	None	13.1	None	29.0	None	25.2	None	24.0	None

The work on the equilibrium experiments was interesting from the point of view that the adsorbed material seemed to be held by two distinct forces. About one-third of the adsorbed phosphate seemed to be held as claimed by Freundlich (3) while the remaining two-thirds seemed to be held in some different way. Analysis showed that it was not at least all as iron or aluminum phosphates. Experiments are now being run to find any further evidence as to just how it is held. Also, experiments are about completed, which show that this phosphate which cannot be leached from the gel with distilled water can be used by a plant in its growth. These results will be reported in a later paper.

SUMMARY

1. Nitrates suffered only slight adsorption while the sulfates, and particularly the phosphates, suffered large adsorption.
2. The order of adsorption of the cations is calcium, magnesium, potassium, while the order in the case of the anions is phosphate, sulfate and nitrate.
3. The time required for equilibrium to be established was a function of the amount of shaking and the rate of adsorption.
4. The adsorption was specific.
5. With solutions of the same salt, the amount of adsorption increased with an increase of concentration.

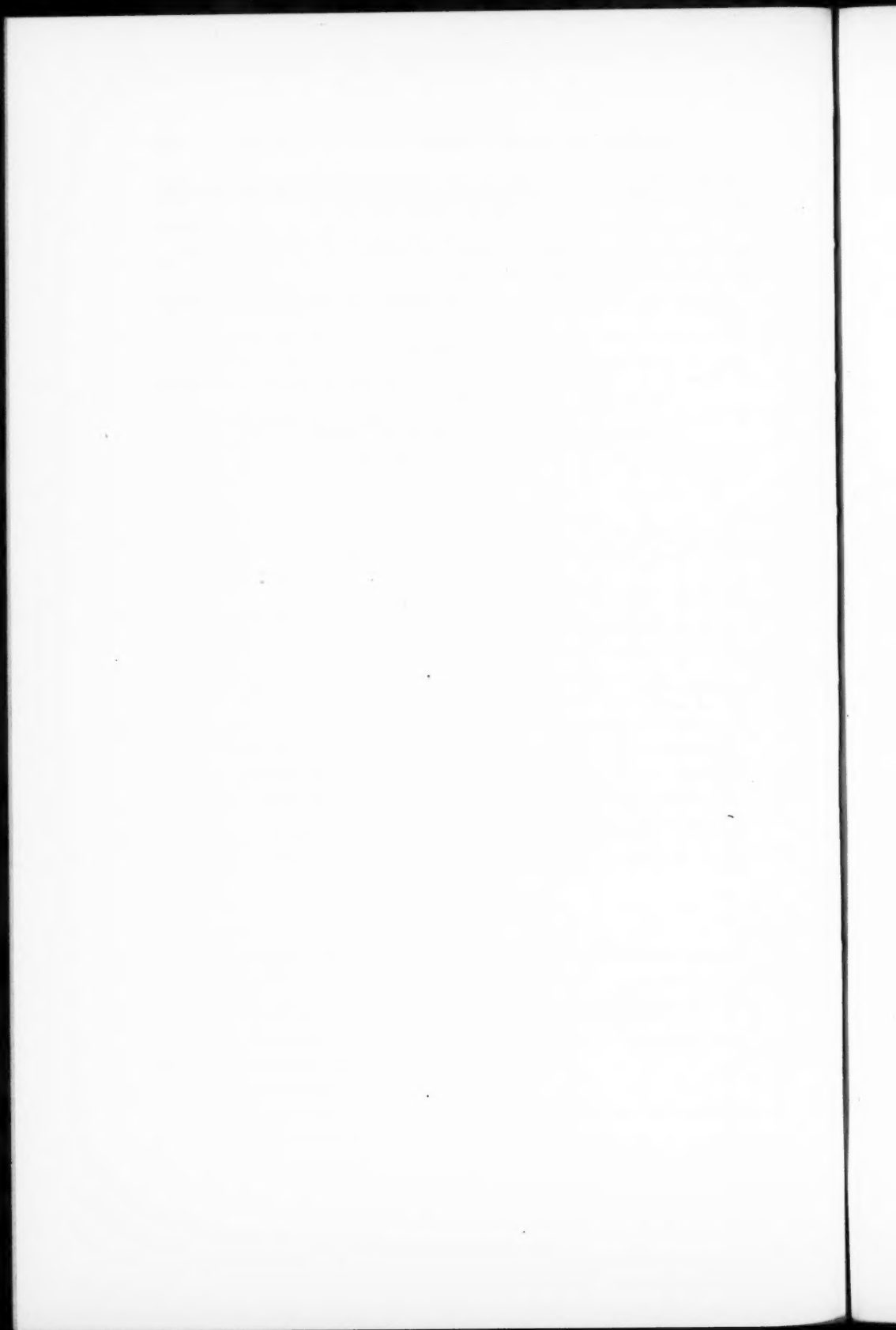
6. The adsorption of a metallic ion depended upon its accompanying negative ion. The converse is true but to a much less degree.

7. The nitrates and sulfates adsorbed by the hydrogels can be entirely leached out by water while only about one-third of the adsorbed phosphates can be removed by leaching with water.

8. Only the water-leachable material showed the adsorption equilibrium law.

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AVAILABILITY OF POTASSIUM IN ORTHOCLASE FOR PLANT NUTRITION^{1,2}

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INTRODUCTION

Chemical analyses show that potassium is always present in soils and, with the exception of peats, mucks, and light soils, in relatively large quantities.

Experiments conducted at the Pennsylvania Experiment Station by Frear and Erb (24) indicate that, in some soils at least, potassium is not only present in considerable quantities but is available to such a degree as to render fertilization with this element unnecessary. In other soils, however, according to DeTurk (21) the potassium normally present is held in such a form that very little is readily available for the use of farm crops. Such soils respond readily to the use of soluble potassium fertilizers, and as a matter of fact, such applications seem to be necessary for maximum crop production.

While the greater percentage of the soil potassium is held in the form of relatively insoluble silicates such as biotite, muscovite, orthoclase, microcline, etc. and their decomposition products, a part is derived from plant residues. If it were not for the latter source, plants requiring large quantities of potassium probably could not reach full maturity owing to the limited amount of the element going into solution from the native minerals. An experiment by Hopkins and Aumer (27) is of interest in this connection. They found that soil freed of acid-soluble potassium would not, at first, support the growth of plants. As all other nutrient materials were supplied to this particular soil, the plants utilized the potassium of the seed, but death occurred soon afterward because the plants were unable to obtain further supplies of this element from the soil. It was found, however, that if these plants were not removed but incorporated with the soil and the process repeated several times, normal growth could be obtained eventually.

The above experiment does not signify, however, that plants are not capable of utilizing potassium directly from the minerals themselves. Lichens readily obtain a foothold on the most resistant potassium-bearing rocks, such as granites. Rocks of this nature compare, in a measure, to the soil freed of available potassium as used in the experiment already mentioned.

¹ The author takes great pleasure in thanking Dr. Firman E. Bear for the many helpful suggestions which he so kindly gave him in the pursuance of this work.

² A thesis submitted to the faculty of the Graduate School of the Ohio State University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, and published as Contribution No. 2 from the laboratories in Agricultural Chemistry, Pennsylvania Experiment Station.

OBJECT OF THESE INVESTIGATIONS

In view of the fact that most soils contain enough potassium to supply the requirements of crop plants for an indefinite number of years, and yet the cost of materials supplying potassium reaches an enormous figure annually, it seems desirable to consider more carefully the possibility of increasing the availability of the potassium normally present in the soil. Since the problem is one which bears directly upon plant nutrition it was thought that more satisfactory results could be obtained by the growth and subsequent analysis of a plant possessing a high potassium requirement in an artificial soil of known composition, the potassium of which would be supplied in the form of one of the common minerals found in soils. By insuring the presence of other essential elements in available forms and in quantities sufficient to render potassium the limiting factor in the nutrition of the plant, such an investigation should give, in a measure, the availability of the potassium from the mineral supplying it, providing, of course, no serious detrimental factors should arise. In addition, it was thought that if certain other organic and inorganic substances would be added in such amounts as not to seriously interfere with the normal growth of the plant, their effect on the availability of the potassium might be noted.

It is clear, however, that such a method of investigation presents its own peculiar difficulties, such as lack of aeration, and the possible accumulation of substances harmful to plant growth due to the lack of drainage of the pots holding the artificial soil. Pots having drainage facilities would suffer a loss of soluble potassium not accounted for by plant analysis, and the same would hold true if the other plant nutrients were replaced from time to time. On the other hand, such an experiment should give comparative results, providing all factors influencing plant growth were controlled, to a greater or less degree, as was attempted in this investigation.

RESULTS OF PREVIOUS INVESTIGATIONS

It has been known for a long time that the ordinary potassium bearing silicates are measurably soluble in water.

This fact has been established as a result of experiments conducted by various investigators among whom may be mentioned the Roger brothers (38), Clarke (13, p. 156), Cushman (15), and Kahlenburg and Lincoln (29). In this connection Cameron and Bell (11, p. 17) declare that water brings about their hydrolysis as evidenced by the alkaline reaction obtained on treating an aqueous solution of the mineral with phenolphthalein. Recently Plummer (37) showed that the solvent action of carbonated water is very much greater than that of distilled water.

The liberation of potassium from its minerals has been accomplished in other ways, e.g., by the use of solutions of ordinary salts. Lemberg (30) and Beyer (7) have demonstrated that various salt solutions produced marked solubility effects on the potassium-bearing silicates.

The investigations cited, and similar experiments performed by André (3), Daubré (17), Johnstone (28), and many others have established the fact that under certain conditions at

least, the potassium minerals are soluble in water, more so in carbonated water, and, if treated with solutions of certain inorganic compounds, their potassium may be replaced.

For a number of years, this problem of the liberation of soil potassium has been attacked in various ways. In 1848 Magnus (33) prepared an artificial soil to which he supplied potassium in the form of powdered feldspar only. With such a medium for plant growth, he was able to bring a crop of barley to complete maturity. Similar experiments were conducted by Aitkin (1), Nilson (34), Ballentine (4) and Feilitzen (22), showing that, under certain conditions, at least, part of the potassium of feldspar could be utilized by certain plants during their growth. Hartwell and Pember (26), however, as a result of extensive experimentation on the use of feldspar in this connection, came to the conclusion that little could be expected from this mineral as a source of available potassium for plant nutrition.

In 1860 Dietrich (18) conducted some experiments to determine the solubility of the soil constituents in various salt solutions. He found that potassium was more readily extracted from the soil by carbonated than by distilled water. Later, Dietrich (19) using 0.05 solutions of sodium chloride, calcium chloride, and calcium hydroxide, found that these solutions dissolved more potassium from soils than did pure water. He also found that solutions of sodium nitrate and sodium carbonate had no apparent effect upon the solubility of the soil potassium.

Fraps (23) claims that sodium sulfate, sodium nitrate or other salts have little effect upon the solubility of potassium in soils, but that lime or organic matter liberates this element to some extent. On the other hand, Lyon and Bizzell (32) place little emphasis on the effect of lime in the liberation of potassium from soils while Wheeler (41, p. 75), in summarizing certain experiments carried on at the Rhode Island Station, concluded that a study of the soils of that state did not justify the assumption that lime is to be considered as an extensive liberant of soil potassium.

PLAN OF THE EXPERIMENT

Description of the materials used

Pure white sand thoroughly leached with tap water and rinsed with distilled water was used throughout these experiments as a medium for plant growth. On analysis it was found to contain but a trace of potassium.

Orthoclase was chosen as the mineral to be used. In order to determine its maximum solubility in water under uniform physical conditions, it was pulverized to such a degree that it would readily pass through a 200-mesh sieve. Twenty-five-gram portions of the powder were transferred to Erlenmeyer flasks of 500 cc. capacity, each containing 250 cc. of distilled water and agitated on a shaking machine. It was found that the solutions contained 28.28 parts per million of potassium when equilibrium was obtained.

Buckwheat was chosen as the plant to be grown for two reasons, first, it is primarily a plant of high potassium requirement and, second, it grows reasonably well under greenhouse conditions.

The potassium content of high grade seeds similar to those planted was found equivalent to 1.16 per cent of their total weight, as determined by the method of Ames and Boltz (2, p. 206).

Earthenware jars were used in these investigations, a half-gallon and a gallon size, to each of which the same weight of sand was added.

The organic and inorganic substances used were chemically pure materials and were found to be practically free of potassium, with the exception of calcium carbonate which contained 1 mgm. of potassium in 25 gm. of the material. Dextrose and starch were chosen in preference to other organic additions mainly because of the fact that they are comparatively free of inorganic material.

A complete nutrient solution, in which the constituent compounds were dissolved and made up to volume separately, was devised. This was found to be acid to phenolphthalein

but alkaline to methyl orange. The weights of the different materials estimated on the water-free basis, the volume of distilled water added, and the amounts of each of the resulting solutions taken for one application are given in table 1.

Distilled water was added to the sand in the jars. Each jar was weighed daily and the water was maintained at a content approximating 14 per cent of the weight of sand. When the nutrient solution was added directly to the jars in the quantities indicated above, the resulting concentration at the optimum water-content of the sand was 36.3 p.p.m. of nitrogen, 51.5 of calcium, 32.7 of phosphorus, 41.7 of potassium, 31.6 of magnesium and a trace of iron.

Solutions of the sodium salts were made, having a volume of such concentration that 10 cc. corresponded to 41.7 p.p.m. of sodium when added to the jars. In like manner solutions of dextrose were made up, just before using, and in such concentration that 10 cc. were equivalent to 100 p.p.m. of this compound.

TABLE 1
Composition of nutrient solution

MATERIAL	AMOUNT	VOLUME	AFFLICTION
	gm.	cc.	cc.
$(\text{NH}_4)_2\text{HPO}_4$	14.4908	8000	10
$\text{CaH}_4(\text{PO}_4)_2$	25.9389	8000	10
$\text{Ca}(\text{NO}_3)_2$	68.5225	8000	10
MgSO_4	99.7879	8000	10
K_2SO_4	9.1661	2500	10
FeCl_3	0.1000	250	1

EXPERIMENTAL

A preliminary experiment was undertaken in order to ascertain the practicability of this kind of investigational work. At the conclusion of this test, a more extended experiment was undertaken along the same lines. On May 26, 1919, the appropriate amounts of sand, alone and with the additions of the insoluble compounds, were weighed out and transferred to each of the 90 jars making nine different series of five duplicate tests each, as shown in table 2.

Fifteen grams of buckwheat were planted after the sand had been brought to its optimum water content. After the plants were well above the sand six uniform plants were selected for growth and the others removed with the exceptions of jars 18 and 20 in which seven plants were accidentally allowed to remain until they had reached such a state of growth that it was considered inadvisable to remove them.

The first application of the nutrients was made on June 2 followed by successive additions on June 9, 16, 23 and 30, and on July 7 and 13. The jars were weighed daily and brought to the optimum water-content, care being taken to prevent undue evaporation by white-washing the interior of the greenhouse roof and by keeping the floors sprinkled morning and afternoon.

On July 14 every plant was severed close to the sand, measured and then placed in a weighed tared envelope with the others of the same jar. After drying, the plants were analyzed, duplicate determinations being made instead of taking a composite sample of each individual treatment.

The data of this experiment are given in tables 3-6.

DISCUSSION OF RESULTS

A factor that affects the growth of plants either advantageously or disadvantageously is that of the reaction of the nutrient medium. In this connection attention is called to the fact that the complete nutrient solution used in this experiment was quite acid in reaction. In addition, it has been stated by Breazeale and LeClerc (9) that plants growing in the presence of compounds such as were used in this solution, render the solution more acid than originally through selective absorption.

While the effect of a nutrient solution moderately acid in reaction is that of hindering the elongations of root systems, this fact in no wise altered the

TABLE 2
Additions to the quartz sand medium in which plants were grown
Each pot contained 2750 gm. sand and other materials indicated

GENERAL TREATMENT	SUPPLEMENTAL TREATMENTS								
	Check	CaCO ₃ (25 gm.)	CaSO ₄ (25 gm.)	NaCl*	Na ₂ SO ₄ *	Dextrose† (0.2716 gm.)	Dextrose (0.2716 gm.) + CaCO ₃ (25 gm.)	Starch (0.2425 gm.)	Starch (0.2425 gm.) + CaCO ₃ (25 gm.)
	jar nos.	jar nos.	jar nos.	jar nos.	jar nos.	jar nos.	jar nos.	jar nos.	jar nos.
Complete nutrients.....	1-2	11-12	21-22	31-32	41-42	51-52	61-62	71-72	81-82
Complete less K.....	3-4	13-14	23-24	33-34	43-44	53-54	63-64	73-74	83-84
Same as 2 plus 25 gm. of ortho- clase.....	5-6	15-16	25-26	35-36	45-46	55-56	65-66	75-76	85-86
Same as 2 plus 50 gm. of ortho- clase.....	7-8	17-18	27-28	37-38	47-48	57-58	67-68	77-78	87-88
Same as 2 plus 75 gm. of ortho- clase.....	9-10	19-20	29-30	39-40	49-50	59-60	69-70	79-80	89-90

* Equivalent to a total of 0.1123 grams of sodium, one-seventh of this amount constituting one application.

† 0.2716 grams, one-seventh of this amount constituting one application.

ability of the plants of jars 1 and 2, which received the complete nutrients, to absorb the potassium supplied them in available form. These plants contained in their tops an average of 92 mgm. of the 112.3 mgm. of potassium supplied. From the data presented in tables 3, 4, 5 and 6 it seems that orthoclase must have exerted a beneficial effect on the nutrient solution as evidenced by yields and amounts of potassium absorbed by the plants of series 1. A greater amount of dry matter was obtained where 50 and 75 gm. of orthoclase were present than where the complete nutrients were supplied, notwithstanding the fact that less potassium was absorbed by the former plants.

TABLE 3
Total yield of dry material

JAR NOS.	GENERAL TREATMENT	SERIES 1—CHECK	SERIES 2—CaCO ₃	SERIES 3—CaSO ₄	SERIES 4—NaCl	SERIES 5—Na ₂ SO ₄	SERIES 6—DEXTROSE	SERIES 7—DEXTROSE + CaCO ₃	SERIES 8—STARCH	SERIES 9—STARCH + CaCO ₃
Ending in		gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
1	Complete nutrients	4.20	4.31	4.08	3.59	4.21	3.86	5.24	3.76	2.55
2		4.33	4.50	5.05	3.89	3.14	4.22	4.39	3.86	3.51
3	Complete less K	0.99	1.31	1.52	1.14	0.57	1.06	1.81	0.58	1.35
4		1.13	1.40	1.37	1.02	1.07	0.90	2.18	0.47	0.63
5	Same plus 25 gm. orthoclase	3.23	4.36	3.84	4.25	3.68	2.29	2.98	1.92	3.27
6		3.58	3.83	4.00	4.23	3.24	2.61	2.17	2.36	2.81
7	Same plus 50 gm. orthoclase	4.36	4.24	5.05	4.65	4.19	3.81	3.38	3.19	4.02
8		4.77	4.88*	5.38	4.82	3.93	3.70	3.60	3.38	4.23
9	Same plus 75 gm. orthoclase	5.24	5.35	5.03	4.88	3.88	4.20	4.10	3.82	3.88
0		5.11	4.87*	4.44	4.30	3.81	4.06	4.08	3.24	3.93

* Seven plants.

TABLE 4
Total potassium absorbed

JAR NOS.	GENERAL TREATMENT	SERIES 1—CHECK	SERIES 2—CaCO ₃	SERIES 3—CaSO ₄	SERIES 4—NaCl	SERIES 5—Na ₂ SO ₄	SERIES 6—DEXTROSE	SERIES 7—DEXTROSE + CaCO ₃	SERIES 8—STARCH	SERIES 9—STARCH + CaCO ₃
Ending in		mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
1	Complete nutrients	89	92	97	91	97	94	106	100	90
2		95	94	111	102	98	102	111	96	106
3	Complete less K	7	8	10	10	8	11	14	8	14
4		10	9	10	8	9	9	18	7	8
5	Same plus 25 gm. orthoclase	24	39	36	36	27	17	23	19	25
6		32	38	35	33	17	22	19	19	22
7	Same plus 50 gm. orthoclase	54	52	65	57	36	32	31	40	44
8		57	61*	69	51	36	31	29	33	37
9	Same plus 75 gm. orthoclase	79	89	78	61	40	43	37	45	52
0		78	91*	74	55	35	43	37	45	43

* Seven plants.

As stated before very little potassium was present in the supplemental materials used, yet the plants of jars 3 and 4 were found to contain an average of 8.5 mgm. as shown in table 4. This absorbed potassium undoubtedly came

TABLE 5
*Average relative weights of dry material**

GENERAL TREATMENT	SERIES 1—CHECK	SERIES 2—CaCO ₃	SERIES 3—CaSO ₄	SERIES 4—NaCl	SERIES 5—Na ₂ SO ₄	SERIES 6—DEXTROSE	SERIES 7—DEXTROSE + CaCO ₃	SERIES 8—STARCH	SERIES 9—STARCH + CaCO ₃
Complete nutrients.....	100	103	107	87	86	95	112	89	71
Complete less K.....	25	31	34	25	19	22	46	12	23
Same as 2 plus 25 gm. of orthoclase.....	80	96	91	100	81	57	60	50	71
Same as 2 plus 50 gm. of orthoclase.....	107	107†	122	111	95	88	81	77	96
Same as 2 plus 75 gm. of orthoclase.....	121	120†	111	108	90	97	96	82	91

* The yield of plants receiving complete nutrients was taken as 100.

† Thirteen plants.

TABLE 6
*Average relative amounts of potassium absorbed**

GENERAL TREATMENT	SERIES 1—CHECK	SERIES 2—CaCO ₃	SERIES 3—CaSO ₄	SERIES 4—NaCl	SERIES 5—Na ₂ SO ₄	SERIES 6—DEXTROSE	SERIES 7—DEXTROSE + CaCO ₃	SERIES 8—STARCH	SERIES 9—STARCH + CaCO ₃
Complete nutrients.....	100	100	113	105	106	106	118	106	106
Complete less K.....	9	9	10	9	9	10	17	8	12
Same as 2 plus 25 gm. of orthoclase.....	30	42	38	37	16	21	22	20	25
Same as 2 plus 50 gm. of orthoclase.....	60	61†	72	58	39	34	32	39	44
Same as 2 plus 75 gm. of orthoclase.....	85	98†	82	63	40	46	40	49	51

* Plants receiving complete nutrients were taken as 100.

† Thirteen plants.

to a great extent from the jars themselves. Not more than 2.5 mgm. was present in the seeds. That this amount represents closely the quantity set free in the other jars as well is indicated by the amount of potassium absorbed by the plants of series 1 grown in the presence of varying amounts of orthoclase. Taking the blanks into consideration it would appear that the tendency of the plants was to absorb a quantity of potassium directly proportional to the amount of mineral added.

EFFECT OF CALCIUM SALTS

The effect of calcium carbonate on the absorption of potassium from orthoclase is shown by the plants of series 2, tables 3 and 4. The average amount of potassium taken up by the plants receiving the complete nutrients in addition to calcium carbonate, i.e., those of jars 11 and 12 was approximately the same as in the absence of the lime salt.

The check plants of this series receiving the potassium-free nutrient solution in addition to calcium carbonate, as compared with those of series 1, showed that no more potassium was absorbed than in the absence of the latter addition. On subtraction of this blank, however, it is evident that more potassium was taken up by the plants from orthoclase in the presence of carbonate of lime. The plants of jars 15 and 16 absorbed an average of 30 mgm. of potassium from the mineral or 10.5 mgm. more than the plants of jars 5 and 6. Where increasing amounts of orthoclase were used in addition to the calcium carbonate treatment, the increased absorption of potassium was almost in direct proportion to the amount of mineral added, and in all probability would have been more nearly so if the extra root system of the additional plants in jars 18 and 20 were taken into consideration.

The reason for the better growth of the plants of this series may be partly due to calcium functioning as a plant nutrient but in all probability most of its effect can be attributed to its neutralizing action on the acidity of the nutrient medium, thereby rendering a more favorable condition for plant growth. In series 1 and 2 it is noted that the increasing growth obtained where orthoclase was present was also accompanied by an increase in the amount of potassium absorbed. In both series, however, greater growth was obtained where orthoclase was present notwithstanding the fact that more potassium was taken up from the complete nutrients. In all probability, the increased absorption of potassium was due primarily to the greater growth of the plants, inasmuch as plants grown under favorable conditions should have a greater feeding capacity than plants grown under conditions less favorable.

That plants grown under favorable conditions would absorb more potassium from orthoclase than those grown in an unsatisfactory medium is evident from results obtained by investigations conducted by Cushman and Hubbard (16), Van Bemmelen (6), DeTurk (21), Beaumont (5, p. 17), and others. Their experiments indicate that very little of the potassium obtained on the hydrolysis of a feldspar goes directly into solution but rather it is held in the colloidal covering of hydrated aluminum silicate surrounding each particle in the form of an absorption compound. Assuming then, that each particle of orthoclase becomes covered with colloidal matter, such a film, according to Beaumont (5), will bring into solution a certain amount of potassium, and under certain conditions this is a fairly constant quantity. If, however, plant roots come into contact with such a film, part of the potassium will be removed and the equilibrium destroyed. The tendency, therefore, would be for more potas-

sium to be made available from the mineral and to replace the amount removed by the plant. If this is true, it would appear that the amount of potassium absorbed from orthoclase depends upon the extent of root development and the greater the development the more of the element absorbed. Such a condition naturally arises where the medium is more favorable for plant growth.

There is a marked distinction between the relative availability of the potassium when supplied as the sulfate or mineral. A study of the plants of the different series as shown in table 4 reveals the fact that all plants receiving the complete nutrients with or without other supplementary treatments absorbed practically all of the potassium, and that this element was taken up regardless of the general character of the plants themselves. This fact indicates that water-soluble potassium can be taken quantitatively from a sandy medium and that the amount absorbed is not dependent upon the relative extent of root development. A further study of these particular plants shows, that those of inferior growth contained relatively more potassium in their tops than those more normal in character. In all probability, where the conditions were less suitable for maximum development those plants had a less extensive root growth and consequently less potassium would be found in the roots and more in the tops. These facts show that if potassium goes directly into solution it may be taken up by plants regardless of their general character and this would hold true for the potassium of orthoclase as well as the sulfate. If no interfering factors were present all the plants grown in the presence of varying amounts of orthoclase would absorb relative quantities of potassium and, if the solubility of this element was affected by certain additions, then the amount of potassium absorbed would indicate the relative efficiency of the various additions in this connection. As such results were not obtained it is clear that certain other factors interfered and in all likelihood one was the colloidal matter of the partly hydrolyzed orthoclase.

The plants of jars 21 and 22 receiving the complete nutrients plus 25 gm. of calcium sulfate are shown to have more potassium in their tops than those receiving the complete nutrients alone or with calcium carbonate. This is probably due to a less developed root system and the excess potassium, instead of being utilized for such growth in the connection, is taken up by the main portion of the plants. Plants absorb more of the essential elements than they ordinarily require and at the same time they manifest a selective absorption in regard to certain radicals. The tendency of a nutrient solution containing calcium sulfate when used for plant growth is to become more acid in reaction due to the fact that calcium is more readily absorbed than the sulfate radical. Pitz (36) has found that small amounts of calcium sulfate greatly increased the extent of root systems but for some reason larger concentration had the opposite effect. While the solubility of calcium sulfate is quite low in distilled water, potassium sulfate, according to Cameron and Bell (12, p. 9) increases its solubility to a great extent. This would result in

more calcium being absorbed and the acidity of the nutrient medium to increase with the possibility of such an increase in acidity being great enough to interfere with normal plant growth.

The plants of this particular series show that those of jars 25 and 26 absorbed more potassium from 25 gm. of orthoclase than was absorbed from the same amount of the mineral through any other treatment. Those of jars 27 and 28 not only absorbed more potassium from 50 gm. of orthoclase than with any other treatment, but gave the highest yield of dry matter of the entire experiment as shown in tables 5 and 6. The nutrient medium in this particular instance must have been of optimum reaction and concentration.

Those plants of jars 29 and 30 grown in the presence of 75 gm. of orthoclase, however, gave a lower yield of dry matter than the plants just mentioned and relatively less potassium was absorbed, undoubtedly because the feeding powers of the plant were impaired to the same extent and by the same causes as stated for the case of the plants of jars 21 and 22; or the action may have been due to an accumulation of dissolved calcium sulfate.

It is evident that under certain conditions calcium sulfate aids in the absorption of potassium from orthoclase but that increased absorption is probably due to the increased growth of the plants under these conditions rather than direct replacement of potassium by calcium from the mineral. This statement is in keeping with those of Hart and Tottingham (25), and Pitz (36). That calcium sulfate under other conditions is somewhat injurious to plants has been proved by Fraps (23), and that calcium sulfate in solution does not liberate potassium directly is indicated by the results obtained in experiments conducted by Briggs and Breazeale (10).

EFFECT OF SODIUM SALTS

As shown in table 6 those plants of series 4 receiving sodium chloride plus the complete and potassium-free nutrients contained the same amount of potassium as was taken up by those plants grown in the absence of this salt. Where 25 gm. of orthoclase were present, however, better growth was obtained and more potassium was absorbed than in the similarly treated plants of series 1 where sodium chloride was absent. This indicates in a measure at least, that where potassium is present in limited quantities this salt may serve as a substitute, increasing the growth of the plants and indirectly causing an increased absorption of potassium from the mineral.

The plants growing in the presence of 50 gm. of orthoclase and sodium chloride were approximately the same, both in yield and the amount of potassium absorbed, as those grown in the absence of this salt.

This was not true, however, of the plants of this series grown in the presence of 75 gm. of orthoclase, as both the yield and the amount of potassium absorbed were decreased by the sodium chloride.

The effect of sodium sulfate was found to be less satisfactory in comparison with sodium chloride. It must be remembered, however, that relatively

greater amounts of this salt was used than the chloride and it is fairly well known, according to different experiments conducted by Hart and Tottingham (25), Fraps (23) and Breazeale (8) that this salt sometimes has an injurious effect on plants. In some instances this harmful action has been ascribed to the concentrations of the medium rather than to an increase in the hydrogen-ion concentration which might arise through selective absorption by the plants themselves.

EFFECT OF ORGANIC MATTER WITH OR WITHOUT CALCIUM CARBONATE

Application of dextrose seriously interfered with the growth and potassium absorption of the plants of series 6 as shown by tables 5 and 6. That such an effect is not altogether unusual has been proved by Lipman and others (31). They found that dextrose applied in a somewhat similar manner depressed the yield of plants.

The too rapid evolution of carbon dioxide, one of the products formed in the decomposition of dextrose, tends to drive out the oxygen from the nutrient solution. According to Snow (39), lack of oxygen seriously interferes with root-hair development of plants, thereby decreasing its absorption powers to some extent. Noyes and Weghorst (35) are of the opinion that carbon dioxide is detrimental to root growth and in fact De Saussure (20) as early as 1804, found that plants grown in pure carbonated water were injured to a considerable extent.

Other acids are also found as decomposition products of dextrose and it was thought that applications of calcium carbonate would tend to neutralize them and so prevent an unsuitable reaction of the nutrient medium. As a matter of fact, such additions failed to exert a pronounced beneficial effect on either the growth of the plants or the amount of potassium absorbed as shown by the data of tables 5 and 6, series 7.

The reasons for these results may be an accumulation of soluble calcium compounds formed by the reaction of calcium with the products of organic decomposition or, perhaps, as the calcium was made available sufficient quantities were absorbed by the plants to seriously interfere with their normal activities. In the latter connection Clevenger (14) found that the hydrogen-ion concentration of the sap of buckwheat plants was lessened in every instance where lime was supplied to the nutrient medium. It is perfectly obvious that a lowering of the concentration of hydrogen-ion would result in affecting the general well being of plants.

Truog (40) found that additions of lime to acid soils sometimes retarded the growth of crops immediately following, such as oats, wheat and corn, which have low lime requirements. He says, however, that this is due to temporary conditions which soon disappear and the lime then greatly benefits these crops as well as those with high lime requirements.

The data concerning the plants of series 8 as shown in tables 4 and 5 indicate that the deleterious effect of starch when used alone on plant growth is more

pronounced than those of dextrose. It is shown, however, where calcium carbonate was used with starch that in a measure at least, the yields and the amounts of potassium absorbed were increased.

From the result of the experiment it is impossible to say whether or not organic matter liberates potassium from orthoclase, as the use of organic substances under the conditions of this experiment shows that such substances seriously interfere with plant growth and thereby obscure their effect on the mineral itself.

SUMMARY AND CONCLUSIONS

This investigation had for its purpose the testing of the rate of availability of the potassium of orthoclase when supplied in finely divided form to buckwheat grown in quartz sand cultures.

Twenty-five-gram portions of the orthoclase, pulverized to pass through a 200-mesh sieve, when subjected to the solvent action of distilled water were found to yield soluble potassium at the rate of 282.2 parts per million at the point of equilibrium between solute and solvent. This was equivalent to 7 mgm. of potassium.

This orthoclase was added in 25-, 50- and 75-gram portions and intimately mixed with 2750 gm. of sand to which the other necessary plant nutrients had been added in available forms.

Availability of the potassium of the orthoclase was estimated from the dry weights of the buckwheat plants and from the amounts of the element absorbed by them when the orthoclase was the only source of potassium as compared to the results secured from the use of water-soluble potassium.

The effects of supplemental additions of calcium carbonate and sulfate, of sodium chloride and sulfate and of glucose and starch on the rate of availability of the potassium of the orthoclase measured as indicated above were also studied.

As a result of these studies the following conclusions seem justified:

1. Fifty-gram portions of orthoclase supplied potassium at a sufficiently rapid rate to satisfy the requirements of 7 per cent larger yields of dry matter than were produced by the complete nutrient solution. With 75 gm. of orthoclase the dry weights of plants were 21 per cent greater than those produced by the use of the complete nutrient solution.
2. The plants grown in pots in which the potassium was supplied as orthoclase contained only 30, 60 and 85 per cent as much potassium for the 25-, 50- and 75-gram portions of orthoclase, respectively, as were contained in the plants grown in the complete nutrient solution.
3. The total amount of potassium available from the orthoclase was in no case as large as that in the nutrient solution but the physiological balance of the solution in the sand culture was apparently favorable to a more economical use of the element.

4. Calcium carbonate and sulfate tended to increase the quantity of available potassium. They also aided in the production of a larger amount of dry matter as long as the lack of potassium was a limiting factor in the growth of the plants.

5. When the lack of available potassium was a limiting factor sodium chloride tended to increase the weights of dry matter but on the whole reduced the amount of available potassium. The effect of sodium sulfate was negative both as to weight of dry matter and amount of potassium absorbed.

6. Dextrose and starch tended to reduce the weight of dry matter and of potassium absorbed. The addition of calcium carbonate to these materials did not materially affect the results with dextrose but resulted both in an increase in yield and of potassium absorbed with starch.

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A COMPARISON OF THE ABSORPTION OF INORGANIC ELEMENTS, AND OF THE BUFFER SYSTEMS OF LEGUMES AND NON-LEG- UMES, AND ITS BEARING UPON EXISTING THEORIES¹

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INTRODUCTION

The primary object of these experiments was to study the selective action of different plants as measured by the proportions in which they absorb different elements from soils and nutrient solutions. Little has yet been done by way of comparing the absorption by different plant species when grown under carefully controlled environmental conditions. Considerable work directly or indirectly concerned with the absorption of inorganic elements by plants, including determinations of the ash content and of the effects of different nutrients upon growth, has recently been reported (4, 5, 6, 11, 12, 14). The composition of barley grown on two different soils was studied at successive stages of growth by Burd (1) and the absorption by barley from a nutrient solution was measured at successive stages of growth by Hoagland (9). In these cases, however, the investigators were not studying the relative absorption by different plant species.

By growing plants in nutrient solutions, a very important environmental factor may be controlled in a manner which was not possible a few years ago, when less was known about such solutions.

For these experiments, it was thought advisable to take plants which under ordinary field conditions are believed to differ considerably in composition and to grow them under more carefully controlled conditions, in order to find out whether the differences are really characteristic, or simply the result of different environments.

It has been quite generally noted that legumes, as a rule, have a higher nitrogen content than non-legumes. This is usually accounted for by the fact that, in the field, legumes probably obtain a larger supply of nitrogen than non-legumes by reason of their symbiotic relationship with nitrogen-fixing bacteria. It has been observed further, by certain workers (14) that legumes and other plants with a relatively high nitrogen content have also a correspondingly high calcium content. Because these differences in composition

¹ This paper forms a portion of a thesis presented in partial fulfillment of the requirements for the degree of Ph.D., University of California. The work was carried out at the suggestion of Prof. D. R. Hoagland.

had been noted, it was considered especially desirable, in studying the selective action of different plants, to compare the absorption by legumes and non-legumes.

A second object of these experiments was to examine the theory advanced by Parker and Truog, regarding calcium and nitrogen relationships in plants (14). According to this theory, the building up of proteins in plants involves the production of by-product organic acids, which are neutralized and precipitated by calcium. Hence the amount of calcium taken up is somewhat directly proportional to the amount of protein or nitrogen built up. Since this involves a question of the relative amounts of calcium and nitrogen absorbed by plants, it was considered that the theory could very well be examined in conjunction with other absorption studies.

That part of the legume nitrogen supply which is fixed by nodule bacteria must almost certainly pass into the plant roots proper in a form which is different from the form or forms in which non-legumes obtain their whole supply. The first product of nitrogen assimilation by legume bacteria and the form or forms of nitrogen assimilated by the plant from the nodules are unknown. However, the fact that legumes grown in nutrient solutions do not absorb their nitrogen in the form elaborated by nodule organisms should hardly affect the absorption of other elements. Strowd (16) stated that an increase in the supply of nitrogen, either from nitrates or nodules, causes an increase in amine and amide nitrogen in the soybean plant, but that this increase is independent of the form of nitrogen supplied. Hence there is no evidence as yet that nitrogen metabolism in the plant follows an appreciably different course when the form of nitrogen taken in by the plant is different, and it is not likely that the requirements for other elements would be affected by the form of nitrogen absorbed. Moreover, in one experiment with peas, described later in the paper, the source of nitrogen was mainly derived from the root nodules.

Another object of the experiments was to study the plant sap of legumes and non-legumes, with special reference to calcium absorption. In connection with the belief that the function of calcium is to neutralize and precipitate organic acids present in the plant and thus avoid an excess of acid in the plant sap, determinations were made of the actual acidities, buffer values, and composition of juices of legumes and non-legumes grown in solutions with a plentiful supply of calcium, and in solutions with a limited supply.

The general type of experimentation was as follows: In nearly all cases, the legumes and non-legumes were grown side by side in nutrient solutions, soil or sand cultures, and the plants or solutions analyzed at various stages of plant growth. The plants for the sap studies were grown similarly and were frozen immediately after harvesting; later they were thawed out, the expressed juice was titrated with the hydrogen electrode, and samples were analyzed for certain elements.

DISCUSSION OF METHODS EMPLOYED

In beginning this work, the different species which were to be compared were grown in separate jars of nutrient solution, and absorption was measured by analyzing samples of the solution taken at intervals. Later the plan adopted was to grow the different species together in each jar, and analyze the plants themselves instead of the solution. In this case, of course, it would be useless to analyze the solution. The advantages and disadvantages of each method will now be considered.

One advantage of growing the plants together, rather than separately, is that the different species must then be growing in exactly the same solution at all times, even when the solution itself undergoes change because of the absorption of ions by the plant. Another advantage of growing the plants together and analyzing the plants themselves, rather than the solution, is that the percentage composition of the different species may then be compared. For certain purposes, it seems better to compare percentages than to compare actual amounts absorbed, because the relative rates of growth of the different species may differ at different periods.

All percentage values in the different tables which follow are based upon the dry weight of the plants and not upon their green weights. If percentages had been based upon the green weights of plant tops, the relative values for the different plants would not have been altered much, since in practically all cases the plant tops compared contained similar percentages of moisture. Of course it would be unreasonable to base any percentages upon the wet weights of the roots, since this depends upon the amount of adhering water, as well as upon their moisture content. These considerations are mentioned since it might be argued that the concentration of the nutrient elements in the plant sap would depend upon the plant's water content.

In interpreting the data obtained by measuring absorption with the two different types of cultures, it will not be possible to compare percentages, because in one case percentages could not be calculated. Ratios of ion equivalents absorbed may be compared because it was possible to calculate these ratios no matter how the absorption was measured. But ratios of ion equivalents absorbed are affected, as shown later, by differences in the solution in which the plants are growing, and may, therefore, be affected by changes in the solution caused by absorption. Evidently, then, ratios obtained by measuring the absorption by different species grown separately are not strictly comparable.

A disadvantage of growing different species together in single containers, as compared to growing them separately, is that a separate lot of plants must be grown for each stage at which the absorption is measured. If plants are analyzed at several growth stages, it means that a very large number of plants must be grown, since variability errors may be large if too few plants are taken for analysis at each stage. When grown separately, of course, nutrient solution samples may be taken as often as desired throughout the whole growth cycle, from one lot of plants.

The possibility of toxic excretions from the roots of plants has often been discussed, and the question was raised as to whether in these experiments one species would excrete a substance from its roots which would be toxic to another species growing along with it. The different species grown together appeared to develop quite normally, however, and there was no evidence of a toxic effect of one upon another.

Evidence has been obtained that plants adjust the reaction of the solution in which they are growing, thus attaining some sort of an equilibrium with it, and it may be that optimum equilibrium conditions for one species are not quite optimum conditions for another species. In this case, it might be impossible for either species to attain equilibrium with the solution if different species were grown together.

However, when the main object of the experiment is to study the relative absorption under a given set of environmental conditions, the advantages of growing the different species separately are certainly outweighed by the advantages of growing them together.

For these selective absorption experiments, plants were chosen which did not differ radically in type of growth, because, for purposes of comparison it is probably well to choose different species which develop at somewhat similar rates, and which come to maturity in about the same length of time. The more nearly alike the different species are in rate of growth the better, no doubt, will be the comparison of their relative absorption of ions at any particular stage of growth. Since it is not probable that any two species follow exactly the same growth cycle, at best plants can only be compared at approximately the same stage, or stages, of growth. It was thought, however, that the plant's composition would change but little throughout a considerable period of vegetative growth if the nutrient solution were maintained somewhat constant in composition.

Details of each experiment will be found attached to the different tables. The number of plants grown for analysis at each stage of growth was fairly large in order to reduce errors resulting from variability. The number taken to make up a composite sample was in no case less than twenty, and in most cases much larger. The importance of errors resulting from the variability of individual plants has been emphasized by Davis (4). Care was taken, also, to change the solutions often enough to avoid complete absorption of any one constituent at any time, except in special cases, as, for example, when a solution of low calcium content was used. A few drops of iron solution were added every three or four days. The importance of these precautions has been emphasized by Hoagland (9, 10).

The compositions of the nutrient solutions employed are given below. "Parts per million" refer to the number of grams of each ion per million grams of solution. Under "relative numbers of ion equivalents" each value given represents the percentage of the particular ion equivalent referred to, in relation to the sum of the five or six different ion equivalents considered in the

table. The advantage of this method of representation is that it shows the number of each of the ions or ion equivalents in relation to the total number of ions or ion equivalents present in the solution, as well as relations between particular ions.

TABLE 1
Composition of different nutrient solutions employed

	Ca	K	Mg	NO ₃	PO ₄	SO ₄
<i>Parts per million</i>						
* Control solution.....	160	185	55	720	105	215
Low Ca solution.....	18	355	5	486	52	100
Low N solution.....	100	100	30	192	134	242
<i>Relative number of ion equivalents present</i>						
Control solution.....	22	13	12	32	9	12
Low Ca solution.....	4	41	2	36	7	10
Low N solution.....	22	11	11	14	19	23

* General nutrient solution used by Hoagland and found adapted to the normal growth of many types of plants, in solution or sand culture.

DISCUSSION OF RESULTS BEARING UPON THE THEORY ADVANCED BY PARKER AND TRUOG

Parker and Truog gathered data from many sources regarding the percentages of calcium, nitrogen, potassium, magnesium and phosphorus in different plants. They then listed the plants in order of increasing percentages of nitrogen, and found that they had, with but few exceptions, arranged them in order of increasing percentages of calcium also, but not in any orderly relationship with the percentages of the other elements. In order to explain this apparent parallel relationship between the amounts of nitrogen and calcium taken up, the theory was advanced that the building up of proteins in plants involves the production of by-product organic acids, which are neutralized and precipitated by calcium, and that practically all of the calcium taken up by plants is utilized in this way.

Before considering experimental results bearing upon this calcium and nitrogen relationship theory, it would probably be well to mention one or two of the possible objections to the theory. In the first place, the soils upon which these plants were grown were unknown to Parker and Truog, and it may have happened that most of the plants containing high percentages of nitrogen were grown on soils rich in calcium. For example, we know that legumes are usually richer in nitrogen than non-legumes, and many farmers consider that legumes must be grown on soils rich in lime. Then there seems to be no particular reason for thinking that protein metabolism would produce more by-product acids than carbohydrate metabolism.

With the object of finding out whether the amount of nitrogen utilized by plants is depressed by a limited supply of calcium, barley and peas are grown together in a nutrient solution containing little calcium or magnesium, but a good supply of the other essential elements, as well as in a balanced nutrient

TABLE 2

Data on barley and peas grown in the control nutrient solution, and in a solution deficient in calcium

CROP	NUTRIENT SOLUTION	Ca	K	Mg	N	P
<i>Percentage (dry weight) composition</i>						
Barley tops.....	Control	<i>per cent</i> 1.02	<i>per cent</i> 4.93	<i>per cent</i> 0.39	<i>per cent</i> 4.65	<i>per cent</i> 1.04
Pea tops.....	Control	1.19	5.19	0.37	4.46	0.87
Barley tops.....	Low calcium	0.74	8.11	0.38	5.75	1.10
Pea tops.....	Low calcium	0.78	7.58	0.31	5.91	0.99
Barley roots.....	Control	0.99	6.46	0.38	4.37	2.00
Pea roots.....	Control	0.95	6.61	1.13	4.18	2.19
Barley roots.....	Low calcium	0.39	8.15	0.54	4.08	1.28
Pea roots.....	Low calcium	0.39	11.02	0.56	4.57	1.43
Barley plants.....	Control	1.01	5.24	0.39	4.60	1.19
Pea plants.....	Control	1.14	5.47	0.53	4.39	1.14
Barley plants.....	Low calcium	0.67	8.08	0.41	5.43	1.14
Pea plants.....	Low calcium	0.70	8.27	0.36	5.62	1.08
<i>Relative ion equivalents absorbed</i>						
Barley plants.....	Control	8	20	5	50	17
Pea plants.....	Control	9	21	6	47	17
Barley plants.....	Low calcium	5	26	5	50	14
Pea plants.....	Low calcium	5	27	4	51	13

Details of experiment

Control solution:

75 barley and 75 pea plants grown 48 days.

Low calcium solution:

75 barley and 75 pea plants grown 33 days.

In both cases, 3 barley and 3 pea plants were grown together in each jar.

solution. Another object of this experiment was to determine whether barley and peas would be affected differently by altering the composition of the nutrient solution. The details of the experiment and the results obtained follow in table 2.

Comparisons of percentage composition (table 2) and comparisons of the relative numbers of ion equivalents absorbed show that barley and peas

resemble each other quite closely in type of absorption. The absorption is changed alike for both by using a different nutrient solution, and evidently the amounts of certain elements absorbed vary somewhat directly as the concentration of those elements in the nutrient solution. Thus barley and peas grown in the low calcium solution contained distinctly less calcium and more potassium, as the solution itself contained less calcium and more potassium. True, the percentages of nitrogen, magnesium and phosphorous apparently did not vary directly as their concentration in the solution, but the amounts of these elements absorbed might be affected by the amounts of other elements absorbed, by the rate of growth, by the frequency with which the solutions were changed, and perhaps by still other factors. The point is that the changed solution affected barley and peas alike.

Most legumes, under ordinary field conditions, contain higher percentages of nitrogen than most non-legumes, and, according to Truog's theory, would therefore require a larger calcium supply for normal growth than non-legumes. But when a nutrient solution was used, the peas absorbed about the same relative amounts of nitrogen and calcium as the barley. When a low calcium solution was used, they both absorbed relatively more nitrogen than before, and distinctly less calcium. This suggests that the amount of calcium absorbed varies with the amount of calcium in solution rather than with the amount of nitrogen absorbed.

Further evidence that the building up of proteins does not necessarily involve the taking up of especially large amounts of calcium, or that the amount of calcium taken up is not proportional to the amount of nitrogen taken up, was obtained from an experiment in which barley and peas were grown together in sand to which a low nitrogen solution was added. The pea plants in two of the 5-gallon crocks used were inoculated, and in two others uninoculated. The details of the experiment and the results are given in table 3.

The inoculated pea plants were larger, and had a distinctly higher nitrogen content than the uninoculated, but not a higher calcium content (table 3). As a matter of fact, the uninoculated plants, with the lower nitrogen content had a slightly higher calcium content than the inoculated, but this difference in calcium is probably insignificant. The difference in nitrogen content, however, is undoubtedly significant. Enough plants were grown to minimize differences resulting from the variability of individual plants; this is emphasized by the close agreement in average weight of plants and percentage composition between the barley check plants grown with the uninoculated peas and those grown with the inoculated peas. Obviously, then, the increased nitrogen absorption by inoculated peas did not involve an increased calcium absorption.

A COMPARISON OF THE ABSORPTION BY BARLEY AND PEAS FROM A SOIL AND A NUTRIENT SOLUTION

Having found that barley and peas grown together in different nutrient solutions absorbed, in proportion to their weights, practically the same amounts

of calcium, nitrogen and other elements, the question arose whether the same would hold true if they were grown together in a soil. It seemed reasonable to suppose that in a solution, diffusion would be so rapid that the solution for both plants must be exactly the same, but in soil, diffusion would be much

TABLE 3

Data on peas, inoculated and uninoculated, and of barley, grown in sand cultures to which a solution deficient in nitrogen was added

CROP	Ca	K	Mg	N	P
<i>Percentage composition</i>					
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Pea tops, uninoculated.....	1.59	5.67	0.47	3.73	0.89
Pea tops, inoculated.....	1.43	5.07	0.50	4.56	1.10
Barley tops, with uninoculated peas.....	1.22	5.47	0.53	3.03	1.07
Barley tops, with inoculated peas.....	1.31	5.74	0.52	3.10	1.14
<i>Absorption per plant</i>					
	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>
Pea tops, uninoculated.....	0.0043	0.0154	0.0013	0.0101	0.0024
Pea tops, inoculated.....	0.0056	0.0200	0.0020	0.0180	0.0044
Barley tops, with uninoculated peas.....	0.0025	0.0112	0.0011	0.0062	0.0022
Barley tops, with inoculated peas.....	0.0024	0.0105	0.0010	0.0057	0.0021
<i>Relative ion equivalents absorbed</i>					
Pea tops, uninoculated.....	13	24	6	43	14
Pea tops, inoculated.....	11	19	6	48	16
Barley tops, with uninoculated peas.....	11	25	8	38	18
Barley tops, with inoculated peas.....	11	25	7	38	19

Details of experiment

Used four 5-gallon crocks filled with pure quartz sand, to which a low calcium solution was added. The 27 pea plants in two of the crocks were inoculated, and the 27 in the other two were uninoculated; this was successfully accomplished by soaking pea seed in a fresh culture of pea nodule bacteria, in one case, and by soaking pea seed in very dilute formaldehyde in the other case. As many barley plants as pea plants were grown in each jar; these served as checks. The plants were grown outside in July and August, 1921, and were 50 days old when harvested. Four changes of nutrient solution were used, the solution being changed by means of a suction apparatus. The average weights per plant were as follows:

	GREEN TOPS	DRY TOPS
	<i>gm.</i>	<i>gm.</i>
Barley with uninoculated peas.....	0.86	0.21
Barley with inoculated peas.....	0.74	0.18
Uninoculated peas.....	1.7	0.27
Inoculated peas.....	3.7	0.39

slower, and it was thought that, owing to differences in the distribution of the roots together with possible differences in carbon dioxide output from the roots, the two plants might be absorbing from different solutions. Barley and peas were therefore grown together in an adobe soil, and the analytical data obtained from this experiment are presented, for the sake of comparison, along with data obtained when these plants were grown for a similar length of time in a nutrient solution.

TABLE 4

Data on barley and peas grown together in the control nutrient solution, and in an adobe soil

CROP	CULTURE MEDIUM	Ca	K	Mg	N	P
<i>Percentage composition</i>						
Barley tops.....	Control solution	per cent 1.02	per cent 4.93	per cent 0.39	per cent 4.65	per cent 1.04
Pea tops.....	Control solution	1.19	5.19	0.38	4.47	0.87
Barley tops.....	Adobe soil	0.67	5.37	0.66	2.88	0.29
Pea tops.....	Adobe soil	1.57	5.93	1.03	3.69	0.37
<i>Absorption per plant</i>						
Barley tops.....	Control solution	gm. 0.0032	gm. 0.0155	gm. 0.0012	gm. 0.0146	gm. 0.0032
Pea tops.....	Control solution	0.0043	0.0186	0.0013	0.0160	0.0031
Barley tops.....	Adobe soil	0.0021	0.0171	0.0021	0.0092	0.0009
Pea tops.....	Adobe soil	0.0056	0.0213	0.0037	0.0133	0.0014
<i>Relative ion equivalents absorbed</i>						
Barley tops.....	Control solution	8	20	5	52	15
Pea tops.....	Control solution	9	21	5	51	14
Barley tops.....	Adobe soil	7	27	10	50	6
Pea tops.....	Adobe soil	13	24	14	44	6

Details of experiment

Control solution:

75 barley and 75 pea plants, grown 48 days. 3 pea plants and 3 barley plants grown together in each jar.

Soil Culture:

2 5-gallon jars used, 16 barley and 16 pea plants in each. Grown 45 days.

Comparisons of the amounts of calcium absorbed show that when barley and peas were grown together in a nutrient solution, the peas contained about 17 per cent less calcium than the barley, and that when grown together in an adobe soil for a similar length of time, the peas contained approximately 135 per cent more calcium than the barley. It should be noted, also, that the amount of magnesium absorbed by peas was much larger than the amount absorbed by barley when they were grown together in this soil, but that they

both absorbed about the same amount of magnesium from the nutrient solution. The other differences between barley and peas grown together in the soil were not as large, but it is interesting to observe that all were in favor of the peas.

Our next problem was to try to find an explanation for this difference in absorption by barley and peas when grown together in a soil, as contrasted with their similar absorption when grown together in a nutrient solution.

One suggestion was that peas grown in soil have more extensive root systems than barley, and thus obtain more calcium. In a nutrient solution, free from solid particles, diffusion is so rapid that a difference in extent of root systems would not be expected to have an appreciable effect, but in a soil where diffusion is relatively slow, the extent of the root system might be an important factor in determining the amounts of the various elements absorbed. It might be argued, however, that if the differences in calcium absorption were wholly the result of the extent of root system, a difference approximately as great for each of the other elements should be expected. This did not occur except in the case of magnesium. Nevertheless, the results might still be explained on the basis of extent of root systems. It is known that ions diffuse at different rates through a soil, and it may be that calcium and magnesium ions diffuse relatively slowly, and thus greater opportunity for absorption would occur with a more extensive root system. The faster moving ions, on the other hand, might come in contact with the smaller root system as rapidly as the plant could absorb them.

Another suggestion was that peas may give off from their roots more carbon dioxide than barley, and that the carbonic acid thus formed would increase the solubility of calcium and magnesium to a greater extent than that of other nutrient elements, insoluble calcium and magnesium compounds being changed to soluble bicarbonates.

A COMPARISON OF THE RELATIVE AMOUNTS OF CARBON DIOXIDE GIVEN OFF BY BARLEY AND PEA ROOTS

The relative amounts of carbon dioxide given off by barley and pea roots were then measured. It should, perhaps, be stated that various other methods of measuring the carbon dioxide output from roots were tried before devising the following simple method, which proved most satisfactory.

One-quart Mason jars were filled up almost to the corks with pure quartz sand, and nutrient solution was added. Six seedlings were planted in each jar, each plant passing through a separate hole in the rubber cork. Through two other holes in the cork glass tubes were inserted just through the cork from above. One was a straight glass tube through which nutrient solution could be poured, and the other was a large-diameter bent glass tube, to the one end of which was attached a flask of standard barium hydrate whenever the carbon dioxide output was to be determined. At these times the open spaces in the cork around each plant were filled with plastic clay, and the tube through which nutrient solution was added was also closed. Two jars of peas and two jars of barley were arranged in this way.

The plants were between 50 and 60 days old when the determinations were made. After making the last carbon dioxide determination, the sand was washed away from the roots, and the plants were weighed. The weights of twelve plants together were as follows:

	GREEN TOPS	DRY TOPS	WET ROOTS	DRY ROOTS
	gm.	gm.	gm.	gm.
Barley.....	46.5	6.1	36.1	3.5
Peas.....	49.9	6.6	36.1	2.0

The barley and pea plants weighed approximately the same, though the dry pea roots weighed less than the dry barley roots.

The unprecipitated barium hydrate was titrated with 0.02 *N* sulfuric acid, using phenolphthalein as the indicator.

	BARLEY		PEAS	
	cc.	cc.	cc.	cc.
0.02 <i>N</i> Ba (OH) ₂ neutralized by CO ₂ in 45 hours.....	21.5	21.3	40.0	51.2
0.02 <i>N</i> Ba (OH) ₂ neutralized by CO ₂ in 90 hours.....	46.0	47.8	96.6	81.0

Here we have evidence that under these experimental conditions, peas gave off from their roots, in proportion to the size of the plants, a great deal more carbon dioxide than barley. The amount of carbon dioxide given off from the roots in a soil probably has a great influence upon the solubility of substances in intimate contact with the roots, and particularly upon the solubility of calcium and magnesium. In a nutrient solution, on the other hand, all nutrients are already in solution, and no such effect could be expected. Thus we have a very probable explanation for the dissimilarity in absorption by barley and peas when grown together in a soil, as contrasted with their similar type of absorption when grown together in a nutrient solution. This, however, does not exclude the possibility that differences in extent of root system are in part responsible for the differences in absorption.

In view of our results obtained with barley and peas grown side by side on a single soil, it seems quite probable that if the plants listed by Parker and Truog were grown in a similar fashion, differences in calcium content such as those shown in their table would still be obtained, but it seems more likely that these results depend upon the relative amounts of carbon dioxide given off by the roots, together with variations in extent of root system, than that they are primarily related to the amounts of nitrogen metabolized by the plants.

It should, perhaps, be mentioned that in Parker and Truog's list of 34 plants, which were arranged in order of increasing content of nitrogen and incidentally of calcium, 13 of the first 14 belong to the grass family, and 10 of the last to the legume family.

In an earlier publication (17), Truog presents evidence to show that plants which have naturally a high calcium content, have a high feeding power for phosphorus in rock phosphate; that is, such plants grow almost normally when their only source of phosphorous is rock phosphate, whereas plants which

have naturally a low calcium content do not grow at all well when their only source of phosphorous is rock phosphate. The explanation suggested was that when carbonic acid reacts with rock phosphate two products are formed, one being CaHPO_4 and the other being $\text{Ca}(\text{HCO}_3)_2$, and that plants with the high feeding power for phosphorous in rock phosphate take up both of these compounds whereas plants with a low feeding power take up only the CaHPO_4 . In this second case $\text{Ca}(\text{HCO}_3)_2$ accumulates in the soil solution and, according to the law of mass action, depresses the concentration of CaHPO_4 , and limits the plant's supply of phosphorous. Now it is undoubtedly true that some ions are taken up by plants more readily than other ions, but it seems improbable that there is a sharp distinction between plants which can take up $\text{Ca}(\text{HCO}_3)_2$ and plants which cannot. It seems more likely that many plants which have naturally a high calcium content and which have greater power than other plants to take up phosphorous from rock phosphate, owe both properties in large measure to the fact that they excrete more carbon dioxide from their roots than other plants.

It is entirely probable that some plants may remove calcium from solution more rapidly than others, because of certain reactions or precipitations occurring in the plant or because of selective powers of the cell. The experiments with beans, to be described presently, suggest that this may sometimes be true. However, since peas and vetch did not show a similar selective action, it is difficult to conclude that legumes in general, or plants with a high calcium content when grown in a soil necessarily have a metabolism of this type.

Reference should, perhaps, be made here to an explanation suggested by Truog for the beneficial effect of lime upon the growth of certain plants, notably legumes (17). The idea advanced was that only calcium in the form of bicarbonate will neutralize and precipitate organic acids formed in the plant. Plants which produce a large amount of by-product organic acids cannot grow normally, therefore, unless calcium in the form of bicarbonate is present in the soil; such plants are benefited by liming because bicarbonates cannot exist in a very acid soil. In these nutrient solution experiments, however, no bicarbonate was present in the solution as first made up, and the legumes grew normally. Of course this would not altogether prove that the plants can grow satisfactorily without bicarbonates, as bicarbonates would soon replace nitrates absorbed from the solution. Experiments conducted by other workers would, however, suggest that bicarbonates are unnecessary. It has been found possible to grow certain legumes satisfactorily in solutions and some soils in which the hydrogen ion concentration maintained is greater than that at which bicarbonates can exist to any extent.²

A COMPARISON OF THE ABSORPTION BY BARLEY AND COMMON VETCH FROM A SOIL AND A NUTRIENT SOLUTION

Another experiment similar to the one in which comparison was made of the absorption by barley and peas grown in solution and in soil, was conducted

² These remarks apply to solutions in which nitrogen is supplied in the form of nitrate.

with barley and common vetch. Vetch was chosen because, in view of the results obtained with peas and barley, it seemed particularly desirable to find out how other legumes would compare with barley when grown in a nutrient solution and when grown in a soil. Because of lack of time only calcium and nitrogen determinations were made. The results, which follow, indicate that vetch and peas resemble each other closely in their absorption from soils and from solutions.

Comparisons of percentages show that when the barley and vetch were grown together in a nutrient solution, they absorbed similar amounts of calcium and nitrogen, but that when they were grown together in a soil, the

TABLE 5
Calcium and nitrogen content of barley and vetch grown together in the control nutrient solution and in an adobe soil

CROP	CULTURE MEDIUM	Ca	N
		<i>per cent</i>	<i>per cent</i>
Barley tops.....	Control solution	1.46	4.93
Vetch tops.....	Control solution	1.53	4.57
Barley tops.....	Adobe soil	0.50	3.45
Vetch tops.....	Adobe soil	0.90	4.28

Details of experiment

Control solution:

60 barley plants and 60 vetch plants grown for 46 days. Barley and vetch grown together. 3 plants of each per jar (1 liter).

Soil culture:

Barley and vetch grown together 46 days. Total of 29 plants each.

vetch absorbed very much more calcium and somewhat more nitrogen than the barley. The probable reasons for this result were discussed in connection with the pea and barley experiment.

DISCUSSION OF OTHER ABSORPTION EXPERIMENTS

In order to study the selective action of barley and peas, as shown by the proportions in which they absorb different elements from a solution which is exactly the same for both, barley and field peas were grown together in the control nutrient solution, and the plants were analyzed at four different stages of growth. The details and figures follow are given in table 6.

It will be noticed, in comparing the four stages, that the relation of ion equivalents was quite different in the final stage from that in the three earlier stages. The potassium and nitrogen percentages were lower in the final stage than in the other stages.

Comparisons of percentage composition (table 6) and of the ratios in which ion equivalents were absorbed, at each different stage, show that barley and

TABLE 6
Data on barley and peas grown together in the control nutrient solution, at four different stages

CROP	AGE days	COMPOSITION						CROP	ION EQUIVALENT ABSORBED				CROP	NUMBER OF SOLU- TION CHANGES	PART OF PLANT	AVERAGE WEIGHT PER PLANT	
		Part of plant	Ca	K	Mg	N	P		Ca	K	Mg	NO ₃	PO ₄			Green or wet	Dry
Barley.....			per cent	per cent	per cent	per cent	per cent	Barley.....	9	20	8	46	17	1400	Tops	gm.	gm.
Peas.....		Tops	0.945	0.00	0.44	3.93	0.87	Peas.....	7	13	6	58	16	620	Tops	0.27	0.031
	24		0.842	1.60	0.37	4.84	0.83									1.01	0.095
Barley.....		Roots	1.152	0.60	0.88	2.61	1.29	Barley.....							Roots	0.12	0.008
Peas.....			0.706	0.46	0.83	5.19	1.32	Peas.....								0.64	0.029
	48		1.024	0.93	0.39	4.65	1.04		8	20	5	50	17	75	Tops	2.88	0.313
Barley.....		Tops	1.195	1.19	0.38	4.47	0.87	Peas.....	9	21	6	47	17	75	Tops	3.12	0.359
Peas.....		Roots	0.996	0.46	0.38	4.37	2.00								Roots	1.04	0.072
	70		0.926	0.61	1.13	4.18	2.19									1.47	0.096
Barley.....		Tops	1.275	0.97	0.44	4.38	0.96	Barley.....	10	23	5	47	15	20	Tops	24.00	2.14
Peas.....			1.003	0.64	0.27	3.10	0.60	Peas.....	10	19	10	45	16	20	Tops	38.70	4.64
		Roots	1.164	0.99	0.43	3.60	1.54								Roots	6.94	0.34
Barley.....			0.904	0.78	2.35	3.47	1.79	Barley.....								17.50	1.02
Peas.....		Tops	1.262	1.80	0.39	1.70	0.91	Peas.....	19	15	8	34	24	20	Tops	29.25	11.10
	140		1.471	1.73	0.33	1.80	0.51		22	13	9	40	16	20	Tops	25.50	7.80
Barley.....		Roots	3.810	0.63	0.21	1.75	0.56	Barley.....							Roots	18.40	0.86
Peas.....			1.061	1.28	0.84	2.69	0.85	Peas.....								20.60	0.86

The 24-day old plants were supported, during growth, on paraffined netting stretched over the tops of 5-gallon glazed crocks. All others were grown in 1-quart Mason jars. In the case of the 48-day old plants, 3 barley and 3 pea plants were grown in each jar, and in the cases of the older plants, 1 barley and 1 pea plant were grown in each jar. All plants were grown in the greenhouse, January to May, 1921. The solution was not renewed right up to the time of harvesting the 140-day old plants, as it has been found that plants maintain their vegetative growth for a very long time, and do not mature naturally unless partially starved towards maturity. The 140-day old plants were practically mature, but the seed formed was small, and was not analyzed separately. At 70 days, the barley plants had, on the average, 5 to 6 strong tillers, but no heads, and the peas had an average of 1.6 tillers which averaged 56 inches in length, and had just begun to blossom. At 48 days old, the barley plants were just beginning to tiller. The barley and pea plants appeared to grow quite normally at all times.

peas in general resemble each other rather closely in type of absorption. Of course, there are a number of exceptions to this statement, but in this connection, attention is called to the following points.

It can hardly be said that there is a difference in percentage of any one element which holds consistently in favor of either barley or peas throughout all four stages.

The roots were more irregular in composition than the tops, and the largest differences in percentage composition between barley and peas, at any one stage, are to be found in the roots. But the roots form such a small portion of the plant that the average composition of the whole plant, in most cases, resembles closely the average composition of the tops.

The average weights of the barley and pea plants were more nearly alike in the cases of the 48-day old and 140-day old plants than in the cases of the 24-day old and 70-day old plants (table 6), and it will be observed that the composition of the barley and pea plants resemble each other more closely in the former cases. The 24-day old plants were small enough to be influenced in composition by the composition of the parent seed.

The calcium percentages of barley and pea plants, or tops, resemble each other rather closely at every stage. The greatest difference in percentage occurred in the case of the 70-day old plants at which time the barley tops then had about 26 per cent more calcium than the pea tops. When grown together in an adobe soil, the pea tops contained approximately 135 per cent more calcium than the barley, whereas when grown together in this nutrient solution, at a similar age (48 days) and weight, the peas contained only about 17 per cent more calcium than the barley.

Thus the results obtained in this nutrient solution experiment bring out no evidence of a characteristic difference between barley and peas in type of absorption.

In order to gain further information regarding the relative absorption of different plants, some work was conducted with beans and barley.

It will be observed that the bean and barley plants have about the same content of nitrogen, magnesium (tops), and phosphorous, but that the content of calcium and potassium differed markedly. Beans have a higher percentage of calcium and a lower percentage of potassium than barley. Also, in this experiment, beans have a distinctly higher calcium percentage than either barley or peas at any one of the four growth stages in the experiment previously described.

The ratio of ion equivalents, in the case of beans, is about 1 of calcium to 1 of potassium. This is shown in two separate experiments (tables 7 and 8) in one of which the computations were based upon the composition of the solution in which the beans were grown, and in the other based upon the composition of the plants themselves. The ratio of ion equivalents absorbed by barley was about 1 of calcium to 2 or more of potassium in this experiment, and in all but the last stage of growth of both barley and peas in the previously

described experiment. It would be unreasonable to compare the ratio of ion equivalents in these young bean plants with the ratio of ion equivalents in the mature barley and peas. Late stages of growth of the beans were not studied.

TABLE 7
Relative ion equivalents absorbed by beans grown in the control nutrient solutions at 2, 4, and 6 weeks old

AGE weeks	Ca	K	Mg	NO ₃	PO ₄	SO ₄
2	22	18	10	22	10	18
4	17	19	10	35	14	5
6	18	18	9	37	11	7

TABLE 8
Data on barley and beans grown together in the control nutrient solution

	Ca	K	Mg	N	P
<i>Percentage composition</i>					
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Barley tops.....	1.60	7.99	0.52	5.04	0.89
Bean tops.....	2.50	4.78	0.57	4.31	0.92
Barley roots.....	0.81	5.92	0.40	4.51	1.65
Bean roots.....	0.86	6.62	1.09	4.75	1.99
<i>Relative ion equivalents absorbed</i>					
Barley plants.....	9	26	6	46	13
Bean plants.....	16	18	7	44	15

Details of experiment

Table 7 refers to "Speckled Cranberry" beans which were grown for a period of 6 weeks in the control nutrient solution. Absorption was measured by analyzing the nutrient solution at intervals of two weeks. Twenty one-quart Mason jars were used and two bean plants were grown in each.

Table 8 refers to barley and "Speckled Cranberry" beans grown for a period of 44 days in the control nutrient solution. Twenty-four one-quart Mason jars were used and 3 barley and 3 bean plants were grown in each. Three changes of nutrient solution were used. The average weights of the plants when harvested were as follows:

	GREEN TOPS	DRY TOPS	WET ROOTS	DRY ROOTS
	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>
Barley.....	2.18	0.28	1.04	0.04
Beans.....	11.57	1.27	4.28	0.23

It will be seen in the last case that the bean plants were very much larger than the barley plants when harvested and analyzed, and the comparison is, therefore, not as satisfactory as when plants which grow at more nearly equal rates are used.

The evidence at hand thus indicates that there is a characteristic difference in the types of absorption of barley and beans in the early stages at least. Beans absorb more calcium in proportion to potassium, from a given solution, than either barley or peas. No distinctive difference in composition with regard to nitrogen, however, was noted.

A COMPARISON OF THE ACTUAL ACIDITIES, BUFFER VALUES, AND COMPOSITION OF THE SAP OF LEGUMES AND NON-LEGUMES

In connection with the belief that the function of calcium is to neutralize and to precipitate organic acids present in the plant sap, and thus avoid

TABLE 9
Composition of plant sap

	NUTRIENT SOLUTION	AGE	GREEN WEIGHT PER PLANT	Ca	K	N
<i>Barley and peas grown together</i>						
Barley top sap.....	Control	days 51	gm. 4.58	p.p.m. 855	p.p.m. 4300	
	Low calcium	51	4.29	495	4250	
Barley root sap.....	Control	51	1.33	100	3520	
	Low calcium	51	1.46	95	2565	
Pea top sap.....	Control	51	6.29	802	4190	
	Low calcium	51	5.68	395	4190	
Pea root sap.....	Control	51	2.69	230	3260	
	Low calcium	51	2.29	155	3550	
<i>Barley and beans grown together</i>						
Barley top sap.....	Control	56	1.31	850	5817	2240
Bean top sap.....	Control	56	8.28	1305	3830	2220

Details of the experiment

The plants for the studies on sap were grown in nutrient solutions in all cases, and in most cases barley and a legume were grown together, as in previously described experiments. The plants were frozen immediately after harvesting. Later they were thawed out, and the expressed juice was filtered on a Büchner funnel, and titrated with the hydrogen electrode. In many cases, samples were analyzed for certain elements (table 9).

an excess of acid, determinations were made of the actual acidities, buffer values, and composition of the juices of barley, peas and beans which had a plentiful supply of calcium, and of others which had had a limited supply of calcium. These experiments with plant sap are intimately related to the previously described absorption experiments, because they are involved in the question of the absorption and function of calcium.

TITRATION OF 25cc. SAP.

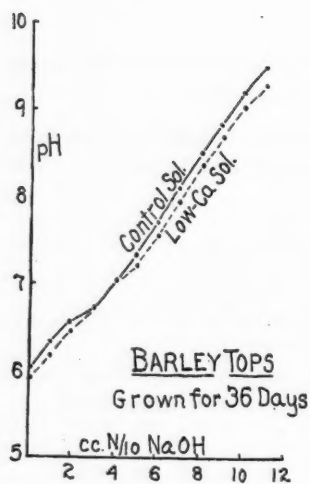


FIG. 1.

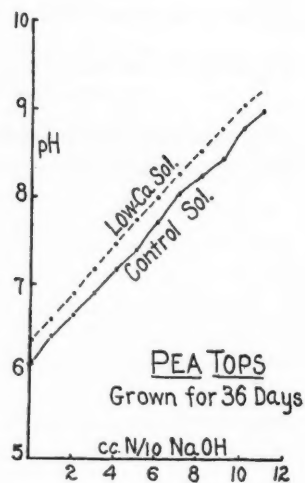


FIG. 2.

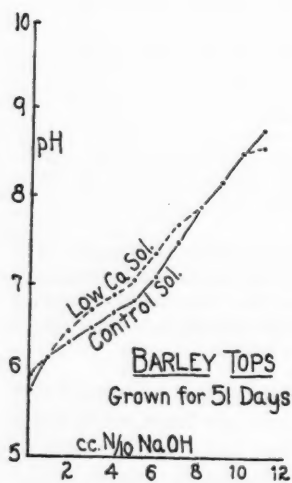


FIG. 3.

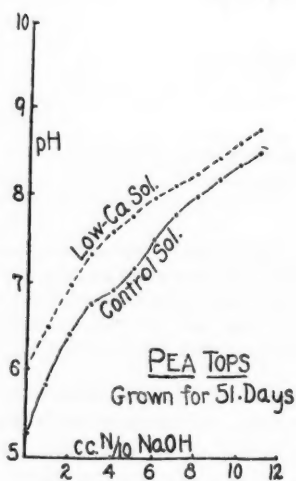


FIG. 4.

TITRATION OF 25cc. SAP.

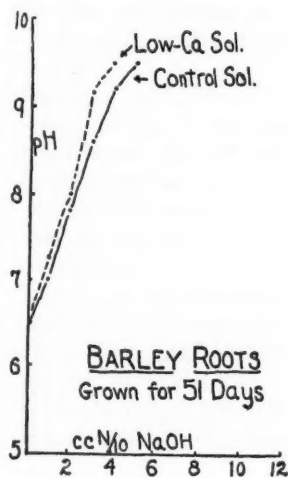


FIG. 5.

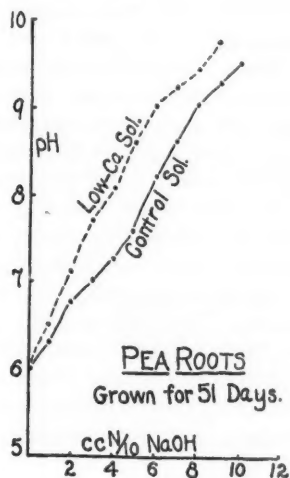


FIG. 6.

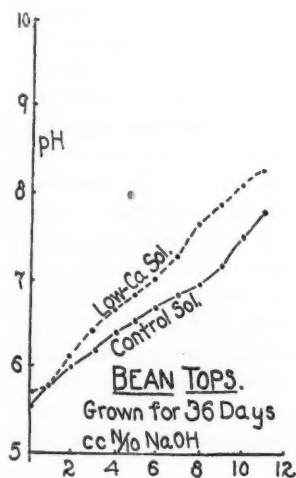


FIG. 7.

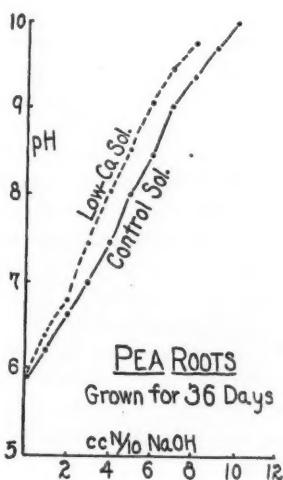


FIG. 8

Strong evidence has been obtained in these experiments that, in the case of barley, peas, and beans, the hydrogen-ion concentration of the plant sap is not appreciably increased by limiting the plant's supply of calcium (figs. 1, 2, 3, 4, 5, 6, 7, 8). The hydrogen-ion concentration was not increased in spite of the fact that analyses proved that there was actually less calcium present in the sap (table 8) and also a less percentage of calcium in the plant, as shown in the earlier experiments.

Though this result may at first seem surprising, it is not difficult to understand why a plant sap containing little calcium might not be any more acid than a plant sap with more calcium. Calcium is not the only base-forming element present in the sap; there is some magnesium and much potassium present also. Salts formed by combinations of these elements with organic acids are undoubtedly present in the sap, and potassium probably replaces calcium to some extent in these organic salts when the ratio of calcium to potassium is decreased, either by an increase in potassium or a decrease in calcium. This might actually produce a more alkaline reaction in the plant sap, because KOH is a stronger base than Ca(OH)_2 , and potassium salts would hydrolyze to a greater extent than calcium salts. As a matter of fact the tendency in these experiments seemed to be in the direction of slightly greater alkalinity as the concentration of calcium decreased in the sap³ (fig. 2 and 4).

Truog and Meacham (19), Haas (7), and Clevenger (2) determined the hydrogen-ion concentration of the sap of plants grown on limed and unlimed soil. Truog and Meacham, and Haas concluded that the sap of limed plants had a tendency towards greater alkalinity than that of unlimed plants. In a number of cases, however, they found that the sap of plants grown on limed soil was more acid than the sap of the same plants grown on unlimed soil. Haas suggested that in these cases, the plants had not absorbed as much calcium from the limed as from the unlimed soil, and Clevenger suggested that the increase in lime stimulated the life process of the plant and caused an increased production of organic acids within the plant. Both suggestions would attribute the increase in acidity to lack of calcium. However it was shown in the experiment previously described that a decrease in amount of calcium actually present in plant sap (or in the plant as a whole) does not necessarily accompany an increase in its hydrogen ion concentration.

Even though plant sap is not rendered more acid by lack of calcium, it is still quite possible that this lack of calcium could produce injury by permitting an accumulation of organic acid salts in the sap. The bivalent ion, calcium, would precipitate organic acids more readily than the monovalent ion potassium, and would thus reduce the concentration of organic acid salts present in the sap.

³ The sap from plants as obtained by the usual methods of expression may not necessarily be identical with the cell sap. It may be questioned whether the reaction of the latter is really subject to appreciable change in a normal plant.

TITRATION OF 25CC SAP.

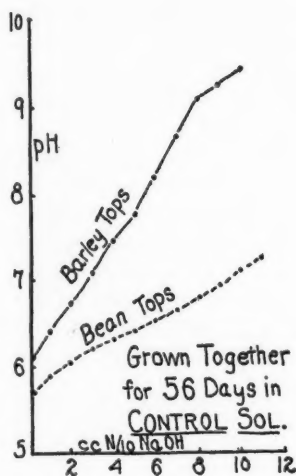


FIG. 9.

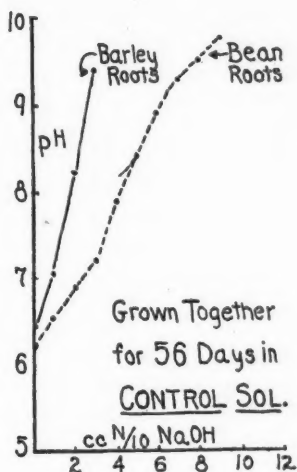


FIG. 10.

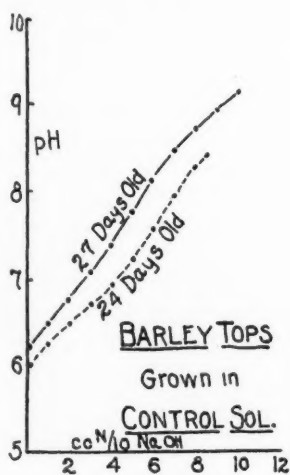


FIG. 11.

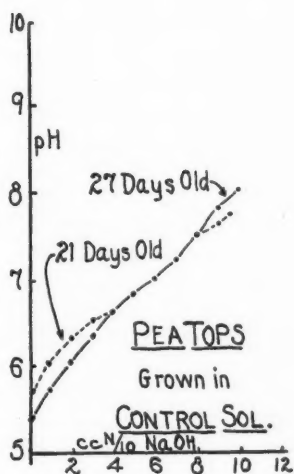


FIG. 12.

Other points which may be noted in the graphs (fig. 1-12) are these:

There was considerable variation in original pH value of the sap of one species, caused, perhaps, by differences in season, age, or other environmental factors.

In most cases the top sap of barley, peas, and beans was more acid than the root sap, but an exception was noted in one experiment with peas, the top sap being more alkaline than the corresponding root sap (fig. 2 and 8).

Barley and pea top juices have approximately equal buffer values (fig. 1 and 2, 3, and 4). Bean top juice has greater buffer value (fig. 9).

Pea and bean root juices have greater buffer values than barley root juice. Pea and bean root juices are much alike in this respect (fig. 5, 6, and 10).

The reactions of the three nutrient solutions used in the different experiments were determined before and after the plants had been grown therein. The original solutions were found to have pH values varying from 4.5 to 5.5, but after the plants had absorbed from the solutions for some time the pH values varied from about 6.8 to 7. Barley, peas and beans grown separately all affected the solutions in this way, the larger plants bringing the solution to this approximately neutral point relatively rapidly. This is in accord with the results obtained by Hoagland, (9), who showed, in his work with barley, that there is a tendency towards the production of a neutral reaction in the nutrient solution, as a result of changes in equilibria caused by absorption.

SUMMARY

1. Comparisons, at four different stages of growth, of percentage composition, and of ratios in which ion equivalents were absorbed, brought out no evidence of characteristic differences in the types of absorption from nutrient solutions by barley and peas, or by barley and vetch.

2. Evidence from two experiments indicates that there is a characteristic difference in the type of absorption of barley and beans in the early stages at least. Beans (speckled cranberry) absorb more calcium in proportion to potassium, from a given nutrient solution, than either barley or peas.

3. Evidently the quantity of calcium absorbed by a plant does not necessarily depend upon the quantity of nitrogen absorbed or metabolized, as has been suggested by other workers. It was found possible to decrease the quantity of calcium absorbed by barley and peas without decreasing the quantity of nitrogen absorbed, by growing the plants in a solution low in calcium. Moreover, it was found that inoculated peas absorbed more nitrogen than uninoculated, when grown in the cultures low in nitrogen, but did not absorb more calcium, though there was plenty of this element available.

4. Peas were found to contain a much higher percentage of calcium than barley, and a considerably higher percentage of magnesium when they were grown side by side in an adobe soil. The differences in percentage of potas-

sium, nitrogen, and phosphorous were smaller, but all were in favor of the peas. Vetch, like peas, was found to have a much higher percentage of calcium than barley, when grown in a soil, but not when grown in a nutrient solution.

5. The quantity of carbon dioxide given off from the roots of pea plants grown in sand cultures was found to be very much greater than that given off from the roots of barley plants of a similar size. This offers a very probable explanation for the fact that pea plants absorb more calcium and magnesium from a soil than barley plants, although they do not absorb more calcium or magnesium from a nutrient solution. In the soil, carbon dioxide would affect the solubility of calcium and magnesium compounds.

6. Evidence was obtained in the case of barley, peas and beans, that the hydrogen-ion concentration of the plant sap was not appreciably increased by limiting the plant's supply of calcium. Analyses proved in these cases that there was actually less calcium present in the sap, and a less percentage in the plant as a whole, as indicated by previous experiments. The buffer effect of barley and pea sap was similar, but was greater in the case of beans.

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SULFUR, CALCIUM, MAGNESIUM AND POTASSIUM CONTENT AND REACTION OF RAINFALL AT DIFFERENT POINTS IN TENNESSEE

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The amount of sulfur precipitated annually at the University of Tennessee Experiment Station Farm has been determined since 1913 in connection with certain lysimeter investigations. The point of collection is located about 1½ miles from the center of Knoxville, a city of extensive manufacturing interests and of a population close to 100,000. From 1913 to 1916 only the total amount for the year was determined. Since January 1917, however, each quarterly precipitation also has been determined. Beginning January 1915, the sulfur precipitation at the Weather Bureau Observatory in the heart of the city has been determined both in annual and quarterly parallels with those at the University Farm. Starting with the fourth quarter of 1918, quarterly and annual determinations have been made also on the rain water collected on a farm near Knoxville and on collections from seven other points in the State. The sulfur precipitations at the University Farm from 1913 to 1922, those at the Knoxville Weather Bureau Observatory from 1915 to 1922 and also the 3-year results at the other Knox County farm are given in table 1. The sulfur data for the seven other points for the years 1919, 1920, and 1921 are given in table 2. These findings have added interest when compared with earlier records contributed by Crowther and Ruston (1), Crowther and Stewart (2), Miller (6), Stewart (8), and more recently (9) by Wilson.

SAMPLING AND ANALYSIS

The samples were collected in standard copper rain gauges or in asphaltum-painted galvanized receptacles of the same dimensions and transferred to glass containers after each rainfall. The clear supernatant rain water was syphoned off from the settled soot and other extraneous materials, or if necessary these were removed by filtration at the time of making the analyses. After concentration, iron and aluminum were removed by ammoniacal precipitation, and calcium and magnesium were determined by the standard methods. The use of Nessler's reagent demonstrated that only fractions of one part per million of nitrogen, as NH_3 , were ever present; while the same finding, with reference to nitrate nitrogen, was obtained by the phenol-disulfonic acid procedure. Silica was never present in amounts sufficient to necessitate its preliminary removal in any of the analytical procedures except in the case of total salts converted to sulfates. Repeated sulfate determinations, with and without preliminary oxidation, established the fact that all soluble sulfur was present as sulfates. Sulfate determinations were made in duplicate, from concentrates equivalent to either 1 or 2 liters

of the original rain water. Total possible sulfates were determined by evaporating the equivalent of either one or two liters of the original rain water with an excess of H_2SO_4 , dissipation of the excess of SO_3 , dissolving of the residual sulfates with HCl , and precipitation as BaSO_4 . Chlorine was determined by titration with silver nitrate in concentrates equivalent to 2 liters of the original rain water. Phosphates were determined by the A. O. A. C. official volumetric method upon 2-liter concentrates. Potassium was determined as K_2PtCl_6 , after the elimination of the trace of ammonia. The reactions were determined quantitatively upon either 100-cc. or 200-cc. portions by titration with 0.05 N acid against both methyl orange and cochineal.

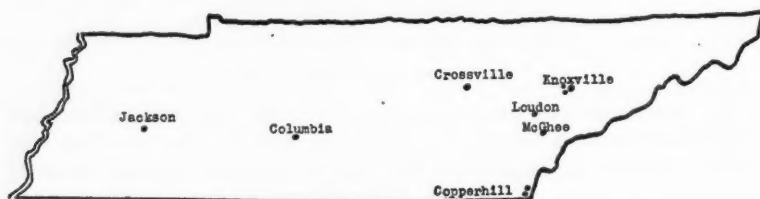


FIG. 1. MAP OF THE STATE OF TENNESSEE, SHOWING THE LOCATIONS OF THE TEN SAMPLING POINTS AT WHICH RAINFALL WAS COLLECTED IN STANDARD 8-INCH GAUGES

SULFUR PRECIPITATIONS

Knoxville, University Farm. The first three years gave 68.7 lbs., 50.6 lbs. and 77.8 lbs. of sulfur per acre surface. The amounts for the first and third years are somewhat above the rather closely agreeing results for the years 1917-1921. The 8-year average of 51.5 lbs. represents non-acid sulfate sulfur. Such an average precipitation of sulfur would be equivalent to an assumed combination of 218.6 lbs. of CaSO_4 . The data show that the sulfur precipitation came heaviest during the winter; that is, in the first and fourth periods. The third quarter yielded the lightest amount in four of the five years of quarterly determinations, the difference being but slightly greater for the third than for the second quarter, in the fifth instance. The sulfur content of the rainfall thus ran parallel with the consumption of soft coal.

Knoxville, Weather Bureau Observatory. The greater amount of soluble sulfate sulfur precipitated within the city is most noticeable for the 1918-1922 period. The total of 175.1 lbs. of sulfur during 1918 causes this year to stand out as abnormal, especially in the first, third, and fourth quarters. The result for the fourth quarter of 1919 was obtained by averaging the data for the corresponding period of the years 1917, 1918, 1920 and 1921, because of the loss of the quarterly sample overnight by freezing. The block of ice saved from this freezing was about one-eighth of the volume of the original sample. It was melted and analyzed for sulfates, yielding 0.3496 gm. of BaSO_4 per liter. While it is possible that this abnormal concentration may represent the composition of the original water, it is more probable that the freezing was so gradual as to effect a concentration of salts in the core represented by the block of ice found on the floor near the broken bottle the following morning.

TABLE I
Quarterly and annual rainfall and sulfur precipitated at three points in Knox County, Tennessee

YEAR	FIRST QUARTER			SECOND QUARTER			THIRD QUARTER			FOURTH QUARTER			ANNUAL		
	Rainfall	BaSO ₄ per liter	S per acre	Rainfall	BaSO ₄ per liter	S per acre	Rainfall	BaSO ₄ per liter	S per acre	Rainfall	BaSO ₄ per liter	S per acre	Rainfall	BaSO ₄ per liter	S per acre
Knoxville, Knox Co., University Farm. Altitude 900 ft.															
1913*	21.58	9.42	9.01	7.36	47.37	.0443*	68.7*
1914*	10.28	8.83	12.68	12.18	43.97	.0412*	50.6*
1915*	11.50	10.56	15.38	16.74	54.18	.0505*	77.8*
1916*	13.61	13.36	14.49	9.33	50.79
1917	20.09	0.0227	14.2	12.26	0.0333	8.9	13.74	0.0138	5.9	5.42	0.0470	14.6	51.51	43.6
1918	11.40	0.0382	13.6	13.73	0.0184	7.9	10.01	0.0272	8.5	11.24	0.0429	15.0	46.38	45.0
1919	16.01	0.0385	19.2	13.82	0.0220	9.5	9.29	0.0240	6.9	18.53	0.0272	8.5	57.65	44.1
1920	13.79	0.0360	15.4	16.79	0.0186	9.7	17.56	0.0130	7.1	10.48	0.0362	11.8	58.62	44.0
1921	11.78	0.0392	12.9	9.10	0.0288	9.0	12.76	0.0162	5.0	9.67	0.0356	11.1	43.31	38.0
Average	14.45	0.0349	15.1	11.99	0.0222	9.0	12.77	0.0188	6.7	11.22	0.0378	12.2	50.42	51.5
Knoxville, Knox Co., Weather Bureau Observatory. Altitude 900 ft.															
1915	10.12	11.28	11.71	15.93	49.04	79.1
1916	10.81	12.03	16.01	8.15	44.55	67.1
1917	23.70	0.0533	39.3	10.14	0.0420	13.2	22.85	0.0277	19.7	5.39	0.1426	23.9	59.72	96.1
1918	10.42	0.2016	65.3	15.02	0.0546	25.5	9.36	0.1263	36.8	12.50	0.1221	47.5	43.79	175.1
1919	12.30	0.0662	25.3	13.33	0.0600	24.9	13.30	0.0352	14.6	11.95	†	27.1	46.30	91.9
1920	12.77	0.0724	28.8	16.71	0.0570	29.6	20.70	0.0170	11.0	9.70	0.752	22.7	55.21	92.1
1921	11.66	0.0642	23.3	8.08	0.0392	12.2	13.75	0.0236	10.1	8.40	0.0462	14.4	40.45	60.0
Average	13.11	0.0915	36.4	12.37	0.0506	21.1	15.38	0.0460	18.4	10.29	0.0965	27.7	48.44	94.5
7 mi. from Knoxville, Knox Co., Ogden Farm. Altitude 900 ft.															
1919	16.01	0.0102	5.1	13.82	0.0136	5.8	9.29	0.0112	3.2	18.53	0.0082	4.7	57.65	18.8
1920	13.79	0.0060	2.6	16.79	0.0150	7.8	17.56	3.2	10.48	4.7	58.62	18.3
Average	14.90	0.0081	3.9	15.31	0.0143	6.8	13.43	0.0112	3.2	14.51	0.0082	4.7	58.14	18.6

* Annual Rainfall collections November to November calculated on same basis.

† Frozen.

TABLE 2
Quarterly and annual rainfall and sulfur precipitated at seven points in Tennessee

YEAR	FIRST QUARTER			SECOND QUARTER			THIRD QUARTER			FOURTH QUARTER			ANNUAL		
	Rainfall	BaSO ₄ per liter	S per acre	Rainfall	BaSO ₄ per liter	S per acre	Rainfall	BaSO ₄ per liter	S per acre	Rainfall	BaSO ₄ per liter	S per acre	Rainfall	BaSO ₄ per liter	S per acre
Copperhill, Weather Bureau Observatory, Polk, Co. Altitude 1600 ft.															
1919	17.76	0.0196	10.8	13.11	0.0428	17.4	12.39	0.0884	34.1	10.33	0.1614	50.2	53.59	112.5
1920	16.93	*	10.8	18.84	0.0396	23.2	21.79	0.0488	67.8	14.29	0.1444	64.2	71.80	166.0
1921	13.33	0.1998	82.8	10.87	0.1408	47.6	15.01	0.1602	74.8	14.43	0.4760	213.6	53.64	418.8
Average	16.01	0.1097	34.8	14.27	0.0744	29.4	16.40	0.0991	58.9	13.02	0.2606	109.3	59.68	232.4
6 mi. from Copperhill, Polk Co. Altitude 1600 ft.															
1919	17.76	0.0705	38.9	13.11	0.0176	7.2	12.39	0.0192	7.4	10.33	0.0358	11.5	53.59	65.0
1920	16.93	0.0188	9.9	18.84	0.0584	34.2	21.79	0.0230	15.6	14.29	0.0246	10.9	71.80	70.6
1921	13.33	0.0334	13.8	10.87	0.0036	1.2	15.01	0.0568	26.5	14.43	0.0878	39.4	53.64	80.9
Average	16.01	0.0409	20.9	14.27	0.0265	14.2	16.40	0.0330	16.5	13.02	0.0494	20.6	59.68	72.2
McGee, Monroe Co. Altitude 850 ft.															
1919	15.44	0.0182	8.7	9.86	0.0188	5.8	6.70	0.0164	3.4	12.52	*	5.1	44.52	23.0
1920	15.42	0.0190	9.1	16.05	0.0104	5.2	21.27	0.0082	5.4	12.21	0.0182	6.9	64.95	26.6
1921	13.98	0.0228	9.9	10.73	0.0108	3.6	13.02	0.0150	6.1	10.76	0.0098	3.3	48.49	22.9
Average	14.95	0.0200	9.2	12.21	0.0133	4.9	13.66	0.0132	5.0	11.83	0.0140	5.1	52.65	24.2

Louden, Loudon Co. Altitude 750 ft.

1919	17.97	0.0124	7.0	10.23	0.0120	3.8	6.93	0.0078	1.7	16.38	*	3.6	51.51	16.1
1920	14.59	0.0146	6.6	17.24	0.0082	4.4	20.11	0.0130	8.1	12.97	0.0068	2.7	64.91	21.8
1921	13.69	0.0182	7.4	10.61	0.0116	3.8	16.40	0.0084	4.3	10.38	0.0138	4.5	51.08	20.0
Average	15.42	0.0151	7.0	12.69	0.0106	4.0	14.48	0.0097	4.7	13.24	0.0103	3.6	55.83	19.3

Crossville, Cumberland Co. Altitude 1850 ft.

1919	13.41	0.0036	1.5	10.27	0.0150	4.8	7.57	0.0036	0.8	16.05	0.0058	2.9	47.30	10.0
1920	17.35	0.0102	5.5	16.34	0.0086	4.4	25.10	0.0018	1.4	10.20	0.0094	3.0	68.99	14.3
1921	16.01	0.0092	4.6	13.96	0.0094	4.1	14.51	0.0062	2.8	8.98	0.0082	2.3	53.46	13.8
Average	15.59	0.0077	3.9	13.52	0.0110	4.4	15.73	0.0039	1.7	11.74	0.0078	3.1	56.58	12.7

Columbia, Maury Co. Altitude 725 ft.

1919	16.55	0.0167	8.6	16.50	0.0106	5.4	10.20	0.0108	3.4	22.55	0.0142	10.0	65.80	27.4
1920	15.50	0.0188	5.8	21.39	0.0082	5.5	12.70	0.0076	3.0	7.75	0.0326	7.9	57.34	22.2
1921	14.33	0.0037	1.6	9.70	0.0158	4.8	17.00	0.0270	14.3	10.70	0.0264	8.8	51.73	29.5
Average	15.46	0.0131	5.3	15.86	0.0115	5.2	13.30	0.0151	6.9	13.67	0.0244	8.9	58.29	26.4

Jackson, Madison Co. Altitude 440 ft.

1919	17.64	0.0582	31.9	11.00	0.0376	12.9	8.34	0.0486	12.6	22.09	0.0230	15.8	59.07	73.2
1920	13.54	0.0526	22.2	13.01	0.0378	15.3	9.18	0.0300	8.6	7.18	0.0438	9.8	42.91	55.9
1921	15.85	0.0398	19.6	10.75	0.0256	8.6	16.01	0.0212	10.6	7.61	9.8	50.22	48.6
Average	15.68	0.0502	24.6	11.59	0.0337	12.3	11.18	0.0333	10.6	12.29	0.0334	11.8	50.73	59.2

* Broken in transit.

If the decidedly abnormal sulfate content of the melted ice were taken as representative, the sulfur precipitation for the fourth quarter of 1919 would appear as 129.9 pounds per acre. This, added to the determined amount of the first three quarters, would give a total precipitation of 194.7 pounds, rather than the reported occurrence of 91.9 pounds for the 1919 annual period. The average of the 7-year period, including the 1919 result above explained, amounts to 94.5 pounds of soluble sulfate sulfur per acre as compared to that of 51.5 pounds as the 8-year average secured at the suburban University Farm.

It has not been generally conceded that fuel consumption is the absolute, or even the paramount, cause of the presence of sulfur in the atmosphere. Lawes, Gilbert and Warington (4) state: "The sulfates of the atmosphere are, according to Angus Smith, chiefly derived from the oxidation of sulphur compounds evolved during the decay of animal matter." And again the same authors (5) state: "The considerable amount of sulphuric acid found in the summer rain points, however, to a further source, most active during high temperatures. This indication is quite in accordance with the opinion held by Dr. Angus Smith, that the sulphuric acid in the rain is largely derived from the products of decay of animal and vegetable matter, which is of course most active in the warmer months." These authors took Dr. Smith's statement from his book *Air and Rain; the Beginning of Chemical Climatology* which was published in 1872.

Ogden Farm, near Knoxville. On this farm, located about 7 miles west of Knoxville, the collections were made by the owner and because of the sale of the property were discontinued after seven quarters. The total amount of sulfur in the rain water was decidedly less than that at the University Farm, which in turn was less than that found in the heart of the city. The Ogden Farm rain water carried very little soot. Thus, with increasing distance from the source of the soot and other solid matter, the occurrence of sulfur was consistently less. This indicates that the major portion of the sulfate sulfur precipitation may be carried by the solid matter rather than as dissolved gases.

Copperhill Weather Observatory. Official rainfall collections were secured from this point, which has an elevation of 1600 feet. The town is the center of an extensive copper industry. In past years vast quantities of sulfur were given off by the open burning of the copper ores and the non-recovery of the evolved sulfur. Extensive areas were devastated of vegetation as a result of the discharge of the acid fumes. Since the enactment of laws necessitating the installation of an acid plant, the evolutions of sulfur have been reduced to the minimum. The data show that the correlation between the domestic or seasonal coal consumption and sulfur precipitation is not so distinct as in Knoxville, a coal burning commercial center. The sample for the first quarter of 1920 was broken in transit and the corresponding figure of 1919 was used in obtaining the total for the annual period. An abnormal discharge occurred during the year 1921 on account of curtailment in the use of transmitted

current for power and the substitution of power generated locally by several large boilers in the Copperhill smelters. For that year there was found a precipitation of 418.8 pounds of sulfur per acre, enhancing the 3-year average to 232.4 pounds.

Near Copperhill, Weather Bureau Observatory. The sampling point is located about six miles distant from Copperhill and it was expected that the sulfur brought down at this location would throw some light upon the aerial diffusion of the somewhat unusual smelter "escapages," at Copperhill. The average of 72.2 pounds for the years 1919, 1920 and 1921 is about half way between the average of the Knoxville Weather Bureau Observatory and that of the University Farm.

McGhee Weather Observatory. This station is about 35 miles southwest of Knoxville and about 65 miles from Copperhill, and has an altitude of 850 feet. It was included along with Loudon, in order to demonstrate, if possible, any relationship between the source of an extensive discharge of sulfur and the direction of the prevailing winds. The town has a population of about 200. The McGhee sample for the fourth quarter of 1919 was broken in transit, and the average of 5.1 pounds for the fourth quarters of 1920 and 1921 was therefore used in obtaining the total for the year 1919. The average of 24.2 pounds for the three-year period is less than half that found at the University Farm. Though none of the quarterly amounts at this station was large, those of the January-March period were consistently higher than those of the other three quarters.

Loudon Observatory. This station is also a small town, of about 1800 inhabitants. It is located about 50 miles from the ore-roasting plant at Copperhill, and has an elevation of 750 feet. The Loudon sample for the fourth quarter of 1919 was likewise broken in transit, and the average figure was inserted in obtaining the total for the year, as in the case of the same period for McGhee. The average annual precipitation of 19.3 pounds per acre was even less than that at McGhee.

Crossville Farm. The samples from this location were collected by one of the coöperative assistants of the University, at a point about six miles from the small town of Crossville. Crossville is located upon the Cumberland Plateau, a sparsely inhabited section and has an altitude of 1850 feet. The amounts of sulfur washed down at this point were the smallest of all of the ten locations. The average for the three years amounts to but 12.7 pounds per acre. The differences between quarterly amounts are not of such magnitude nor consistency as to warrant special stress.

Columbia Station Farm. This source of sampling is located upon the Middle Tennessee Experiment Station Farm, about two miles from the city of Columbia. A side-line railroad passes through the farm. A quarterly comparison does not show any striking relationship between season and the amounts of sulfur brought down. The smallest amount happens to be credited to the

first quarter of 1921, while the largest amount was obtained in the period of July, August, and September of the same year. The average for the 3-year period amounts to 26.4 pounds of sulfur per acre.

Jackson Station Farm. The collections made at this point were secured from the West Tennessee Experiment Station, about two miles from the city of Jackson, in the Mississippi Valley. A branch-line railroad passes through this farm also. The average for the first quarter of each of the three years is about twice that of the average of each of the other three quarters. These latter averages are rather consistent. The annual average for the three years shows a precipitation of 59.2 pounds per acre. It was rather surprising to find so high an average—one greater than that of the University Farm, adjacent to Knoxville—especially since the prevailing winds are not from the town toward the station.

REACTION OF THE RAIN WATER

Each sample of rainfall was examined as to its reaction to common indicators. The averages of titrations for each quarter for the several years are given in table 3. The figures represent cubic centimeters of 0.05 *N* acid required to neutralize a liter of the rain water, both methyl orange and cochineal having been used as indicators. The titrations against methyl orange are consistently higher than those made with cochineal in all periods and for all sampling points. It was anticipated that the amounts of SO_2 evolved from the combustion of soft coal used throughout the area under observation would produce an acid-reacting rain water. However, such did not prove to be the case. In the 320 titrations made in duplicate, not one failed to show alkaline toward methyl orange, while the same was true also, except in three instances, where cochineal was used. In one of these three cases neutrality was shown to cochineal, while a mere trace of acidity was found in the other two instances.

The dry combustion of bituminous coal produces SO_2 , which may be readily detected under conducive atmospheric conditions. The ash, however, both residual and evolved, is distinctly alkaline from the presence of alkali and alkali-earth combinations. Nevertheless, the prevailing conditions of fuel combustion are such as to preclude the neutralization of the volatile acid gas by the preponderance of dry alkali and alkali-earth bases until the solid and gaseous phases are brought into intimate contact through solution in the rainfall, either during precipitation, or after collection in the gauges.

In searching for parallel reaction determinations, we have found only the results of Crowther and Ruston (1). These workers report free acidity amounting to 20.05 pounds of H_2SO_4 as an average annual precipitation near Leeds during the years 1906–1909. The rain water acidity reached the high mark of 41.4 parts per million during the foggy month of December, 1908. Methyl orange was used as an indicator against 0.01*N* alkali. They conclude: "The results bear unmistakable evidence of the fact that the impurities have their origin largely in the combustion of coal, this being the most obvious source of the acid which occurs in such appreciable quantities in the rain." On the other hand, in the same paper the findings at Leeds are shown to have been entirely different. At this point a total of 1886

TABLE 3
Alkalinity determinations, as averages of 1919, 1920 and 1921 rainfalls, collected at 10 different points—titrations with 0.05 N HCl—methyl orange and cochineal as indicators

QUARTERS	KNOXVILLE WEATHER BUREAU		UNIVERSITY FARM		NEAR KNOXVILLE		COPPER HILL		NEAR COPPER HILL		LOUDON		MCHEE		CROSSVILLE		COLUMBIA		JACKSON	
	0.05 N acid		0.05 N acid		0.05 N acid		0.05 N acid		0.05 N acid		0.05 N acid		0.05 N acid		0.05 N acid		0.05 N acid		0.05 N acid	
	Methyl orange	Coch- ineal	Methyl orange	Coch- ineal	Methyl orange	Coch- ineal	Methyl orange	Coch- ineal	Methyl orange	Coch- ineal	Methyl orange	Coch- ineal	Methyl orange	Coch- ineal	Methyl orange	Coch- ineal	Methyl orange	Coch- ineal	Methyl orange	Coch- ineal
First.....	3.35	1.35	5.00	2.65	3.50	3.00	4.00	1.75	4.50	1.00	8.15	4.35	7.85	4.35	7.15	3.65	4.65	1.25	5.50	2.50
Second.....	3.85	1.50	4.85	3.85	6.00	3.75	4.75	2.75	9.15	5.70	4.85	2.35	6.15	3.35	5.35	2.50	3.35	1.00	2.85	1.15
Third.....	3.85	1.50	5.65	3.35	2.00	0	5.85	3.50	13.85	10.15	7.15	3.85	5.85	3.85	3.65	0.85	5.35	2.15	3.65	1.35
Fourth.....	2.50	0.75	4.35	2.15	2.00	0	40.00	17.05	27.00	22.15	6.00	3.50	4.25	1.25	4.35	0.85	5.00	1.25	5.50	3.25
Average for annuals.....	3.39	1.28	4.96	3.00	3.38	1.69	13.65	6.26	13.63	9.75	6.54	3.51	6.03	3.20	5.13	1.96	4.59	1.41	4.38	2.06

pounds of suspended matter fell upon an acre surface during the year, and of this amount 1113 pounds was ash. The authors state, "At this station (Leeds Forge), indeed, the rain was in some cases appreciably alkaline in reaction."

Later, Crowther and Stewart (2), offer findings obtained at 14 stations within a short radius of Leeds. Of 153 samples collected at seven different points 140 were either neutral or distinctly alkaline to methyl orange, congo red, and litmus, while the remaining 13 samples were acid. Finding but a fraction of the total sulfur in unoxidized form, an alkaline rainfall, and citing the conclusions of Herbig (3) to the effect that not more than one-hundredth of the volatilized sulfur leaves the chimney as SO_2 , Crowther and Stewart (2) offer the conclusion: "It is possible that, contrary to the commonly held opinion, the smoke arising from the combustion of coal under industrial conditions may in some cases contain its sulfur not mainly as sulfur dioxide, but almost entirely in the form of sulfate."

According to Richards (7), "Rainwater is very nearly saturated with oxygen when its temperature as collected is below 15°C ," and, "When the temperature of the rain is above 15°C the dissolved oxygen is always below saturation, occasionally as much as 25 per cent." In addition, the tendency of finely divided base-impregnated soot and prevalent dust to absorb gases affords further oxidizing and neutralizing possibilities. Oxidation may also be accounted for, according to Lawes, Gilbert and Warrington (4), by atmospheric hydrogen peroxide, and since this compound "is evolved when turpentine, and possibly other bodies, are oxidized in the air, the neighborhood of a pine forest should be favorable to the formation of nitric acid" (and sulfates)¹ "in the atmosphere." As stated in description of methods of analysis, we found no unoxidized sulfur dissolved in the cumulative samples at the time of analysis. Thus, in the case of the Tennessee precipitations, the rapid diffusion of SO_2 , the excess of solid alkaline material in the smoke, and aerial oxidizing agencies were apparently responsible for complete oxidization of the soluble sulfurous content of rainwaters of alkaline reaction. This is in decided contrast to the marine-influenced rainfall found in England, where a maximum parallel of 380 pounds of SO_2 and 70 pounds of chlorine and a minimum parallel of 128 pounds of SO_2 and 40 pounds of chlorine per acre per annum, with about one-fourth of the total sulfur "in other forms oxidizable to sulfate."

CALCIUM AND MAGNESIUM IN RAINFALL

Little attention seems to have been paid to the basic-element content of rainfall. Lawes, Gilbert and Warrington (4) found but 4.0 parts per million of hardness in a total solid-matter content of 28.0 parts per million, as determined upon 22 samples "from washed gauge" at Rothamsted. "By 'hardness' is understood the total lime and magnesia in water, expressed in parts of carbonate of calcium." Analysis of a composite collection of 47 samples of rainwater from the unwashed gauge gave a total hardness of 4.8 parts per million and a total-solids content of 36.6 parts per million. Again, from 7 samples of dew and hoar-frost the same authors found an average of 19.0 parts per million in an average total-solids occurrence of 48.7 parts per million. Miller (6) compiled an extensive bibliography of 125 references to rainfall data in which Marggraf is cited as having found lime along with nitric acid and chlorine in 1749-1750, confirmed by Bergman, in both rainfall and snow.

It was known that SO_2 is given off at both Knoxville sampling points as a result of the combustion of soft coal. As previously stated, such a discharge may be detected readily by its odor, at times when conducive atmospheric conditions prevail. Consequently when it was found that the rain waters were not acid and that lime and magnesia were present in considerable quantities, further information was sought.

Seven of the quarterly collections from the Knoxville Weather Bureau Observatory and six of those of corresponding periods from the University

¹ (and sulfates) inserted by authors.

Farm were analyzed for lime and magnesia. The amounts of CaO and MgO found, in terms of BaSO₄, and also the amounts of BaSO₄ found in the determinations of total sulfates, are given in table 4.

As previously stated, it seemed possible that the evolved acid gas might be oxidized by aeration and by atmospheric ozone and hydrogen peroxide, bringing the dissolved oxidized sulfur into contact with small particles of limestone dust and basic silicates which would function as neutral-

TABLE 4

*Sulfates accounted for in rainfall by direct determination of calcium and magnesium and assignment of difference to alkali sulfates**

YEAR	COLLECTION PERIOD	WHERE COLLECTED	TOTAL BaSO ₄ DETER- MINEO PER LITER	BaSO ₄ EQUIVA- LENT OF DETER- MINED CaO PER LITER	BaSO ₄ EQUIVA- LENT OF DETER- MINED MgO PER LITER	BaSO ₄ PER LITER UNAC- COUNTED FOR BY CALCIUM AND MAGNE- SIUM SULFATES	PER CENT OF DETER- MINED SULFATES ASSIGNED BY DIFFER- ENCE TO ALKALI SULFATES*
			gm.	gm.	gm.	gm.	per cent
1917	April-June	Knoxville W. B.	0.0420	0.0271	0.0093	0.0056	13.3
1917	July-Sept.	Knoxville W. B.	0.0277	0.0121	0.0064	0.0092	33.2
		University Farm	0.0138	0.0029	0.0064	0.0045	32.6
1917	Oct.-Dec.	Knoxville W. B.	0.1426	0.0478	0.0162	0.0786	55.1
		University Farm	0.0470	0.0154	0.0052	0.0264	56.1
1918	Jan.-March	Knoxville W. B.	0.2016	0.0391	0.0145	0.1480	73.4
		University Farm	0.0382	0.0087	0.0075	0.0220	57.6
1918	July-Sept.	Knoxville W. B.	0.1243	0.0233	0.0075	0.0935	75.2
		University Farm	0.0272	0.0108	0.0087	0.0077	28.3
1918	Oct.-Dec.	Knoxville W. B.	0.1221	0.0208	0.0197	0.0816	66.8
		University Farm	0.0429	0.0121	0.0174	0.0134	31.2
1919	Jan.-March	Knoxville W. B.	0.0662	0.0150	0.0208	0.0304	45.9
		University Farm	0.0385	0.0100	0.0156	0.0129	33.5
Average of all determinations.....			0.0719	0.0196	0.0119	0.0411	46.3

* Disregarding determined traces of Al, Fe and NH₃

izing nuclei in the formation of rain drops. It is undoubtedly true that such nuclei are to be found in the atmosphere because of the evolution of ash and because of the use of limestone in the construction of suburban roads. If such an explanation were to be accepted, our calcium and magnesium results would lead to the conclusion, that limestone or dolomitic limestone dust particles were always present in amounts greater than those necessary to neutralize the evolved acid. Furthermore, the excess of alkali-earth dust particles above the amount combined with the evolved acid would be washed

down mechanically. The filtered and unfiltered rainfall carried the same amounts of lime and magnesia, indicating that all soluble calcium and magnesium salts were dissolved either during the precipitation or as a result of the suspension of the soot in rain water during the quarterly period of collection. It was thought that the suburban farm precipitation, which was lower than the city collection in sulfates, would run higher in total lime since the sampling point was adjacent to limestone roads and closer to the road level. But with the increasing amount of sulfates in the heart of the city where the streets are asphalted, and where the collection point was more than a hundred feet above the road level, increased amounts of dissolved neutral calcium and magnesium salts were found. That is, coincident with sulfate increases, there also occurred a distinct increase in dissolved alkali-earth bases.

The average of the BaSO_4 equivalents of determined CaO , table 4, represents 26.1 per cent of the total sulfates. In nine of the 13 samples, the amounts of lime found were greater than the amounts of magnesia present, in terms of chemical equivalence. The average amount of magnesia found in the 13 quarters accounts for 16.6 per cent of the corresponding average for the determinations of the sulfate radical. It is evident, therefore, that a large part of the precipitated sulfate radical occurs in combination with the alkali-earth bases.

In this connection, the washing of the atmosphere by the rainfall at the Knoxville Observatory was studied for the 3-month period of April, May and June, 1918. The total composite precipitation of 15.02 inches during the quarter yielded 0.0546 gm. of BaSO_4 per liter. In addition to this collection the first $\frac{1}{4}$ -inch and the second $\frac{1}{4}$ -inch of each daytime precipitation were collected and analyzed separately, without including the soot which was more abundant in the first fractional composite. The first $\frac{1}{4}$ -inch yielded 0.2262 gm. BaSO_4 per liter; the second $\frac{1}{4}$ -inch, only 0.0902 gm. While it might be contended that this difference was due to the fact that the evolved sulfurous gases had been washed from the atmosphere before they had diffused to the higher altitudes, the same reasoning would also apply to the evolved sulfate-impregnated solid matter of the smoke.

A somewhat related finding, that of Frankland (Sixth Report of the River's Pollution Commission, 1874), has been reported by Lawes, Gilbert and Warrington (4). Anticipating rain, the gauge was cleansed at 11:30 a.m. and the collections made at 3 p.m. and 4:30 p.m. A total solid-matter content of 40.8 parts per million was found in the first sampling, while but 29.4 parts were found in the second collection. The total nitrogen decreased from 1.43 parts per million to 0.69, while the chlorine decreased only from 1.0 part to 0.8 part per million.

It seems logical to conclude, therefore, that the amounts of soluble lime, magnesia and sulfates found in rain waters are determined by their mechanical diffusion to the atmosphere, as components of soot and fine dust.

DIRECT BaSO_4 DETERMINATIONS AS COMPARED WITH TOTAL POSSIBLE
SULFATES

During the years 1919 and 1920 the direct BaSO_4 determinations upon the collections from the 10 sampling points were compared with those determined after all salts were converted to sulfates. An excess of H_2SO_4 was added to 1- or 2-liter portions, which were then evaporated and ignited. The residue was taken up with HCl , filtered, and the increased combined sulfates determined as BaSO_4 . The direct sulfate determinations and those found subsequent to the sulfate conversions are given in table 5. In every case the BaSO_4 -equivalent, after sulfate conversion, is greater than the corresponding direct barium sulfate determination. An average of 0.0341 gm. of BaSO_4 equivalents is obtained from 36 direct determinations upon the rainfall concentrates, as against 0.0951 gm., representing a similar average for total possible sulfates. These determinations show a rather wide range of proportions between direct and possible sulfates in the several samples, and indicate the occurrence of molar combinations between bases and acid radicals of less combining weight than that of SO_4 . The amounts of carbonates or bicarbonates indicated by the titrations could not account for this difference, assuming all alkalinity as attributable to non-volatile bases.

OCCURRENCE OF CHLORIDES AND PHOSPHATES

From comparisons between the total possible sulfates as BaSO_4 , and the summation of the calculated barium sulfate equivalents of the direct CaO and MgO determinations and those from the K_2O determinations later reported, there is still a considerable difference unaccounted for. This might probably be assigned almost entirely to sodium sulfate derived from sodium chloride in the rain waters. It was, therefore, deemed advisable to establish the occurrence of both chlorides and phosphates.

Attributing the rather heavy occurrence of chlorine as being ". . . principally furnished by the sea, fine spray of salt water being carried long distances by high winds," Lawes, Gilbert and Warrington (4) state: "In a small extent chlorides may also be furnished by combustion of fuel." In a later publication, (5) the same authors account for the excess of chlorine brought down during the winter months by stating: "The large excess of chlorides found in winter rain is probably due in great measure to the chlorides volatilized during the combustion of fuel; the excess in question is too uniform to be dependent chiefly on the action of strong winds blowing from the sea; it is also remarked in calm months as well as in stormy weather. Exceptionally high results are, however, probably due to storms."

One-liter samples of the two collections from the Knoxville stations were therefore concentrated in duplicate for the determination of chlorides and also phosphates precipitated during the first quarter of 1922. The analyses demonstrated the merest trace of phosphates in each case. However, the

TABLE 5
Sulfates in rainfall as compared to determined total possible sulfates, when all dissolved bases present were converted to sulfate combinations, in terms of grams of BaSO_4 per liter

YEAR	QUARTER	AS TO ANALYSIS	KNOXVILLE UNIVERSITY FARM	KNOXVILLE WEATHER BUREAU	ODDEN FARM 7 MILES S. E. KNOXVILLE	COOPER HILL OBSERVATORY	NEAR COPPER HILL	MCREE OBSERVATORY	LOUDON OBSERVATORY	CROSSVILLE FARM	MIDDLE TENNESSEE STATION FARM	WEST TENNESSEE STATION FARM
			gms.	gms.	gms.	gms.	gms.	gms.	gms.	gms.	gms.	gms.
1919	2nd	Present	0.0220	0.0600	0.0136	0.0428	0.0176	0.0188	0.0120	0.0150	0.0106	0.0376
		Possible	0.0584	0.0822	0.0220	0.0800	0.0372	0.0490	0.0620	0.1990	0.0518	0.0850
1919	3rd	Present	0.0240	0.0352	0.0112	0.0884	0.0192	0.0164	0.0078	0.0036	0.0108	0.0486
		Possible	0.0422	0.0532	0.0196	0.1024	0.0418	0.1698	0.0418	0.0660	0.0350	0.1056
1919	4th	Present	0.0272	0.3496*	0.0082	0.0358	0.0058	0.0142	0.0230
		Possible	0.0460	1.1922*	0.0600	0.0400	0.0356	0.1502	0.0690
1920	1st	Present	0.0360	0.0724	0.0060	0.0188	0.0190	0.0146	0.0102	0.0188	0.0526
		Possible	0.0706	0.0834	0.0112	0.0232	0.0628	0.0346	0.0278	0.0342	0.0788
Average		Present	0.0273	0.1293	0.0098	0.0656	0.0229	0.0181	0.0115	0.0087	0.0136	0.0405
		Possible	0.0543	0.3528	0.0282	0.0912	0.0355	0.0939	0.0461	0.0821	0.0678	0.0846

* Melted ice.

amounts of chlorine proved to be appreciable. For the first quarterly composite of 1922, 1.45 cc. of 0.1 *N* AgNO₃ was required for titration of 1 liter of concentrate of the University Farm rain water and 2.95 cc. for that from the city. If these results were taken as representative the average annual precipitation of 51 inches, would wash down 98 pounds of sodium chloride per acre at the University Farm, as compared with 199 lbs. for the city. In corresponding chlorine determinations upon the samples collected during July, August and September 0.40 cc. of 0.1 *N* AgNO₃ for the University Farm and 0.675 cc. of city bureau, respectively, was required for titration. On the basis of 51-inch annual rainfall these determinations would give sodium chloride precipitations of 27 pounds and 45.6 pounds for the University Farm and city, respectively. Assuming the average of the first and third quarters to be representative of the averages of the four quarters there would be an annual precipitation of 62.5 pounds of sodium chloride at the farm and 122.3 pounds in the city. These figures represent about the same proportion that was found for the average soluble sulfate sulfur precipitations at the two points. It is quite apparent from these results that the evolution of chlorides is closely related to the evolution of soot and ash. The chlorine determinations were made for only two quarters and may not be representative of the average composition for the annual period. While not conclusive in showing the absolute amounts of chlorine brought down, the results serve as intended in confirming the assumption of the occurrence of sodium as sodium chloride and being complementary to those of the bases in accounting for the differences between soluble sulfates and total possible sulfates.

POTASSIUM AND SODIUM IN RAINFALL

The direct calcium and magnesium determinations of table 4 were calculated to their respective BaSO₄ equivalents, in order to determine by difference what proportion of the direct sulfate determinations could be assigned hypothetically to the sulfates of these two alkali-earth bases. Only the local collections were so analyzed, since the quantity of each transported collection was limited. Table 4 shows that the difference between the BaSO₄ determination and the corresponding sum of the BaSO₄ equivalents varied from 4.5 mg. to 148 mg. The aggregate of calcium and magnesium fails to account for the amount of SO₄ found in every instance. The results show a considerable range from a maximum of 86.7 per cent to a minimum 24.8 per cent. As an average of 13 alkaline rain waters, 42.7 per cent of determined sulfate radical was accounted for by assuming that all calcium and magnesium occurred as sulfates leaving 57.3 per cent to be accounted for by other bases. The meagerness of ammonium sulfate in the rain water was determined by analysis. The soluble salts of iron, aluminum and manganese were also present only in very minute quantities.

Since the data of table 4 indicated that the differences between the determined sulfates and the calculated sulfates may be assigned jointly to sodium

and potassium, direct determinations of potassium were made upon the first two quarterly samples collected at the University Farm and at the Knoxville Observatory. Total sulfates were determined as before and the calcium, magnesium and potassium occurrences were calculated to their respective BaSO_4 equivalents, as given in table 6. Potassium salts were also found in a sample from Copperhill, but this collection was not of sufficient volume to permit of the complete analytical procedure which was carried out upon the other four rain waters. The occurrence of potassium was more uniform than either that of calcium or magnesium. The total sulfate content of the Weather Bureau sample of the first quarter was found to be nearly three times that of the University Farm collection. However, the proportions of potassium in the two samples were found to be in close agreement. In the second quarter the total potassium content of the city precipitation was considerably greater than that of the farm rain water, but the proportions of potassium were not widely divergent. On the basis of the half-year average of potassium content, the average annual precipitation of soluble potassium salts for eight years has amounted to 9.2 pounds of K_2SO_4 per acre. A similar calculation from the 7-year period data for the Weather Observatory gives an annual K_2SO_4 precipitation of 14.3 pounds per acre.

Thus, for each pound of soluble sulfur washed down upon an acre surface, approximately .18 pound of K_2SO_4 was precipitated at the University Farm, while a corresponding proportion of 0.15 pound of K_2SO_4 was found at the observatory in the city. After allowing for hypothetical sulfates from the direct determinations of calcium, magnesium and potassium, an average difference of approximately one-third may be attributed to sodium, since the possibility of lithium occurrences may be considered as negligible.

AMOUNT OF SOOT IN RAIN WATER AT KNOXVILLE

The foregoing results demonstrate a close parallel between the amounts of sulfur found in the rain waters and the commercial and domestic coal consumption, that is, a relation between the occurrence of soluble sulfates and the amounts of soot and ash evolved from the combustion of bituminous coal. It was thought desirable to ascertain something relative to the amount and composition of the soot found in the rain water. This may not necessarily represent all of the deposited soot. But discharged solids are a source, if not almost the entire source, of the dissolved sulfates and bases of rain water. The determinations of the absolute amounts of soot which are washed down during each season would involve a special study, and the use of specially constructed equipment. It may be well however to determine what amount of soot may be expected in rain waters before considering its composition. The amounts of soot present in the rain water collections from the University Farm and in the city were determined for the second quarter of 1922. In a 12.5-liter sample from the University Farm 0.1830 gm. of soot was found, equivalent to 0.0146 gm. per liter, or 168.6 pounds per acre in a precipitation

TABLE 6
Sulfates accounted for in first 6 months of 1922 rainfall by direct determinations of calcium, magnesium and potassium and assignment by difference to sodium and other bases

COLLECTION PERIOD	WHERE COLLECTED	TOTAL BaSO_4 PER LITER		BaSO_4 EQUIVALENT OF DETERMINED CaO PER LITER		BaSO_4 EQUIVALENT OF DETERMINED MgO PER LITER		BaSO_4 EQUIVALENT OF DETERMINED K_2O PER LITER		BaSO_4 EQUIVALENT ACCOUNTED FOR BY CaSO_4 , MgSO_4 AND K_2SO_4 PER LITER		BaSO_4 EQUIVALENT ASSIGNED BY DIFFERENCE TO Na_2SO_4 AND OTHER SULFATES PER LITER	
		Gram	Per cent of total SO_4	Gram	Per cent of total SO_4	Gram	Per cent of total SO_4	Gram	Per cent of total SO_4	Gram	Per cent of total SO_4	Gram	Per cent of total SO_4
January-March.....	{ Knoxville W. B. University Farm	0.0914	26.2	0.0240	6.3	0.0058	29.1	0.0266	61.6	0.0350	38.3	0.0350	38.3
		0.0326	14.1	0.0046	20.9	0.0068	27.6	0.0090	62.6	0.0122	37.4	0.0122	37.4
April-June.....	{ Knoxville W. B. University Farm	0.0258	30.6	0.0079	17.4	0.0046	26.7	0.0069	75.4	0.0194	24.6	0.0064	24.6
		0.0167	27.6	0.0046	12.6	0.0021	35.3	0.0059	75.4	0.0126	24.6	0.0041	24.6

of 51 inches per annum. In the case of the City Weather Bureau sample, 16 liters of rain water yielded 0.3005 gm. of soot, or 0.0188 gm. per liter, equivalent to 217.2 pounds per acre in an annual rainfall of 51 inches. The quantities given represent the amounts suspended in the rainfall, rather than the total amounts which may have fallen upon an acre surface.

COMPOSITION OF A SAMPLE OF UNLEACHED SOOT

The amounts of soot found in the rain water collections were not sufficient for analysis of sulfates and bases which may not have been dissolved from the soot flakes during the process of precipitation or the period of storage. Total sulfates were determined both in the filtered collections and in the water containing the suspended soot; but, because of the small proportion of soot to rain water, no consistent differences could be detected. Since it was not feasible to differentiate between the total and soluble sulfates and bases contained in the small amount of soot carried by the rain water, some unleached chimney soot was obtained for analysis. It might well be stressed that the total amounts of the solid products of combustion brought to the soil surface are probably considerably in excess of the amounts indicated by the rain gauges, unless precautions be taken to insure that all solid material precipitated over the surface of the collection apparatus is retained in the water samples. At times, large quantities of dry soot may be observed falling in the vicinity of much coal consumption during dry weather. It is, of course, problematical how much of this dry deposition may be dispersed by winds. The form and surface area of the rain water gauges have considerable bearing upon the amounts of solids in the collections. Lawes, Gilbert and Warrington (4) give data relative to the rainfall collections of two large oblong gauges, 6 feet by 7 feet 3.12 inches, embracing a surface area of .001 acre, as compared with those from an ordinary 5-inch circular copper gauge. Over a period of 28 years the large gauges gave a consistently greater collection of aqueous precipitation, equivalent to an average of 9.8 per cent. The disparity is most pronounced during the winter, which is the period of greater soot deposition. The authors state: "Thus a heavy snow-fall is much better retained by the large gauge than the small; the deposits of mist, dew and hoar-frost are also distinctly greater with the large gauge." It is then quite probably true that the same holds also for the deposition of dry soot, and that our own small gauges do not record the full amounts of solid material brought down.

The bituminous coal soot used for analysis was collected from a domestic boiler flue and could not be considered as absolutely comparable with the soot discharged into the atmosphere. The material discharged from the stack would have the maximum of carbonaceous matter and the minimum of the heavier ash, while the unexpelled flue soot would probably have a larger proportion of the heavier ash. The data of table 7 may be considered only as indicative of the composition of solid material carried off from the combustion of bituminous coal and brought to the soil surface by washing of the atmos-

phere and by gravity precipitations. The reaction of the soot was determined by agitating 5 gm. with 300 cc. of distilled water and permitting 20 hours additional contact before filtration and titration with 0.05 *N* acid. The entire extract required 2.7 cc. of 0.05 *N* acid to effect neutralization against methyl orange. On the basis of the amounts of soot contained in the rain waters for the first quarter of 1922, this would mean only 0.12 lb. of water-soluble alkaline material, expressed as CaCO_3 , in the case of the farm precipitation and 0.15 pound at the observatory in the city.

The acid-soluble composition was determined by hot digestion of a 25-gm. charge with aqua regia. After 8 hours' digestion and two evaporations with HCl, the residue was taken up with dilute HCl, filtered and the filtrate made to a volume of 1 liter. Aliquots of 100 cc., a 2.5-gm. charge equivalent, were then used for determinations of calcium, magnesium, potassium, iron-aluminum-manganese, and sulfates. The slightly alkaline aqueous extraction obtained in the reaction determination was utilized in the determination of

TABLE 7

*Analysis of alkaline chimney soot—*aqua regia* digestion for 8 hours aqueous digestion overnight*

SOLVENT	TOTAL BaSO_4 FOUND	CALCIUM AS BaSO_4 EQUIVA- LENT	MAGNESIUM AS BaSO_4 EQUIVA- LENT	POTASSIUM AS BaSO_4 EQUIVA- LENT	CARBONATES		$\text{Fe}_2\text{O}_3 -$ $\text{Al}_2\text{O}_3 -$ Mn_2O_4
					CaCO_3	BaSO_4 equivalent	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Acid.....	8.57	21.89	2.21	2.85	0.27	0.63	13.06
Water.....	1.77	11.26	0.89	1.49	0

water-soluble sulfates. Water-soluble calcium, magnesium and potassium were determined by the analysis of a filtered aqueous solution obtained by overnight contact of 10 gms. of soot in a volume of 400 cc. The filtrate and washings were made to a volume of 500 cc. and aliquots representing 1.5-gm. charges of soot were used for duplicate determinations of calcium and magnesium. Potassium was determined as K_2PtCl_6 upon aliquots equivalent to 1 gm. of soot. The results of the aqueous and acid digestion analyses are given in table 7. In order to facilitate comparison with the rain water results, the soot digestion data are likewise given as BaSO_4 equivalents which were used in computing the total sulfates, sulfates calculated from determinations of calcium, magnesium and potassium and for sodium by difference. It will be remembered that, in the case of the rain waters, the hypothetical sulfate totals of the directly determined elements calcium, magnesium and potassium were never sufficient to account for the totals of determined amounts of the sulfate radical. The reverse is true of the acid extract from the soot. The water-soluble BaSO_4 equivalent amounted to but 1.77 per cent, while the acid oxidation-digestion gave a corresponding equivalent of 8.57 per cent. The acid-soluble calcium proved to be equivalent to 21.89 per cent in terms of BaSO_4 equivalence. On the same basis, 2.21 per cent and 2.85 per cent

could be attributed to magnesium and potassium, respectively. On the other hand, the water-soluble BaSO_4 equivalents of calcium, magnesium and potassium were found to be but 11.26 per cent, 0.89 per cent and 1.49 per cent, respectively. No trace of either iron or aluminum was found in the slightly alkaline aqueous extract. In connection with the alkalinity determinations which demonstrated a paucity of alkali carbonates, these results suggested the possibility of the presence of considerable amounts of the alkali-earth carbonates. However, such was proved not to be the case. A boiling digestion with 0.5 *N* acid gave a CaCO_3 equivalence of only 0.27 per cent or a BaSO_4 equivalence of 0.63 per cent. These analyses indicate that considerable quantities of non-carbonaceous ash, most probably siliceous, are present in the flue soot. The bases of the non-carbonate ash were tightly locked; for, in spite of the alkalinity of the dry soot, the iron pipe from which it was obtained had been attacked as though by an acid and ferrous sulfate was

TABLE 8

Hypothetical depositions of sulfur, calcium, magnesium, potassium and $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Mn}_2\text{O}_4$ per acre from soot suspensions in 51 inches of rainfall calculated from data of tables 6 and 7

PLACE	TOTAL BaSO_4	CALCIUM AS BaSO_4 EQUIVA- LENT	MAGNESIUM AS BaSO_4 EQUIVA- LENT	POTASSIUM AS BaSO_4 EQUIVA- LENT	CARBONATES		$\text{Fe}_2\text{O}_3\text{-}$ $\text{Al}_2\text{O}_3\text{-}$ Mn_2O_4
					CaCO_3	BaSO_4 equiva- lent	
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
University Farm.....	14.2 (3.0*)	36.9	3.7	4.8	0.5	1.1	22.0
City Weather Bureau.....	18.6 (3.8*)	47.5	4.8	6.2	0.6	1.4	28.4

* Water-soluble.

indicated by taste. During periods of no heat and condensation of moisture there was apparently an oxidation of sulfur compounds and formation of acid salts most probably of iron, the $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Mn}_2\text{O}_4$ content of the soot amounting to 13.06 per cent.

SULFUR AND BASES BROUGHT DOWN BY DRY SOOT

As previously noted, considerable quantities of dry soot are often deposited. Analyses of dry chimney soot indicate that not all sulfurous and basic materials carried by the rainfall-soot are in forms which permit of their solution during precipitation, or while standing in the quarterly-collection containers. Applying the soot data of table 7 to the amounts of soot found in the two quarterly rain water collections, and assuming those collections to be representative of the 51-inch average annual precipitation, the pounds per acre data of table 8 are obtained. These figures indicate that the actual sulfur precipitations, and more particularly the wash-down of lime and the ampho-

teric elements, are apt to be somewhat greater than the soluble amounts found in the rain water. Furthermore, gravity precipitation of dry solids augments the amount of sulfur and bases brought to the soil surface. The large excess of basic elements over sulfate and carbonate radicals, together with absence of appreciable basicity, the mere traces of phosphates and the chlorine content, lead to the conclusion that the soot-carried bases are most probably present as silicates. The approximate ratio of 5 parts of total sulfur to 1 part of water-soluble sulfur establishes the fact that the amount of precipitated non-sulfate sulfur varies directly with the amount of the solid soot which may fall in the dry form or along with the rain water. The same is true of ferric, aluminic and manganic oxides, for we have found but traces of the salts of these three elements dissolved in the quarterly rainfall collections.

PRACTICAL SIGNIFICANCE

The results of this study serve to refute some of the viewpoints which have been commonly held relative to the effect of sulfur precipitations upon soils and plant growth in commercial centers, other than those where sulfur is evolved from smelter operations or chemical manufacture. It has been held that sulfur evolutions from coal produce an acid rainfall which depletes the soil of lime and other bases, thereby causing acidity. The writer has known of computations made to show the tonnage of lime required to offset the precipitation of supposed acidity throughout a state, on the assumption that the sulfur evolved from coal combustion, or rather destructive distillation was in the acid combination. The layman has likewise insisted that corrosion of gutters and other exposed metal surfaces is due to this assumed acidity of rain water. Our findings do not support such conclusions. The consistent results upon the reaction of the rain waters at different points and the excess of soluble bases over the soluble acid radicals, indicate that soils are not more depleted of bases, nor made more acid by rainfall than they would be if the precipitations were of pure water. Furthermore, in the case of the two locations, Knoxville and the University Farm, the amounts of calcium, magnesium, potassium and sulfate sulfur reach such proportions as to be considered of some possible manurial value. There is certainly just as much justification for the assumption that the rainfall components are beneficial, as that to the contrary.

SUMMARY

Analyses were made quarterly of the rain water collected at 10 different points in Tennessee.

The 8-year average of annual soluble-sulfate sulfur precipitations at the University Farm was 51.5 pounds per acre. The 7-year average in the heart of the city was 94.5 pounds. The 2-year average 7 miles from Knoxville was 18.6 pounds. Three-year averages at seven other points were as follows:

Copperhill, 232.4 pounds; near Copperhill, 72.2 pounds; McGhee, 24.2 pounds; Loudon, 19.3 pounds; Crossville, 12.7 pounds; Columbia, 26.2 pounds and Jackson, 59.2 pounds.

From duplicate titrations of over 300 samples it was found that every sample was alkaline to methyl orange, while slight acidity was indicated by cochineal in only two instances.

Considerable amounts of calcium and magnesium were found in all of the seven samples from the Knoxville Observatory and the six from the University Farm which were analyzed for these elements. Forty-two and seven-tenths per cent of the soluble sulfates were accounted for by those two elements, as the average from the 13 samples, 26.1 per cent by calcium and 16.6 per cent by magnesium.

Determinations were made upon the samples from all ten sampling points for the sulfate content and the sulfates that would be present if all dissolved bases were combined with the sulfate radical. As an average of 36 duplicate determinations, the sulfates found proved to be but 35.9 per cent of the possible.

Chlorine determinations and tests for phosphate were made upon two quarterly samplings from the two Knoxville collection points.

Sodium and potassium combinations were first determined jointly by difference between total sulfates and those of calcium and magnesium. Potassium was later determined directly. The totals of potassium, calcium and magnesium calculated to sulfate equivalents, established the fact that considerable sodium sulfate was present in the analyzed samples.

The potassium content of rain water was rather uniform. About 30 per cent of the sulfates found were accounted for by this element.

The amounts of suspended soot in certain rain waters were determined.

The water-soluble and acid-soluble composition of unleached soot were given. The former was, on the average, about one-half of the latter.

The relation between the deposition of sulfur, calcium, magnesium, potassium and sodium brought down by gravitation of dry soot and that washed down was considered.

It was pointed out that most of the soluble sulfates found in the rain waters have been dissolved from solid matter and that the volume of such discharged into the atmosphere is the primary factor governing the concentration of sulfates in the rain water.

As a practical application of the findings reported, it is believed that, under the conditions studied, the rainfall carrying sulfurous materials can not be assumed to be more active than pure water in producing acid soils.

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